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FOREWORD

Environmental protection efforts are increasingly directed towards preventing adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, management or engineering tools are developed for assessing and controlling adverse environmental effects of non-irrigated agriculture and of silviculture.

To meet the nation's food production needs, modern agriculture will continue to rely on the application of fertilizers and pesticides. In recognition of this, research continues to be directed toward delineating the fate of these materials after their initial beneficial application. The project described in this report evaluates the movement of several herbicides in the water and sediment being lost from two agricultural watersheds. These analytical data may also serve as a basis for developing and evaluating models of pesticide transport in soils and agricultural landscapes.

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ABSTRACT

Patterns of runoff and sedimentation observed on two watersheds in Michigan are described in relation to weather conditions at different seasons of the year. An assessment is made of sources of variation in pesticide analysis for soil cores taken during the period May 1973 through September 1974 from the two watersheds. A number of relationships to methodology, chemical species, topography, soil conditions, and weather are identified. Criteria are given for assessing down-slope movement within and between sampling segments and movement within the profile. A detailed description is given of weather and watershed conditions associated with wintertime runoff events on the larger watershed and with major spring and summer events on both watersheds in 1975. Emphasis is placed on characterizing boundary conditions at the beginning of each event in relation to weather sequences that preceded it. Only portions of the data set, stored at the Environmental Research Laboratory, Athens, GA, were used in these evaluations. However, important features of soil, topography, management, and weather are identified in relation to useful variation in the data. The described relationships should be helpful in interpreting and modeling data from these watersheds for both pesticides and nutrients.

The detailed descriptions of soils, topography, instrumentation, operational procedures, and management given in this report as background for interpreting the pesticide data also apply to the nutrient data obtained under EPA Grant No. R-802974-01-0. These nutrient data will be summarized and evaluated in a separate report.

This report was submitted in fulfillment of Grant No. R-800483 by Michigan State University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 23, 1972, to October 31, 1975, and work was completed as of June 30, 1976.

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SECTION I

SUMMARY

Soils, topography, instrumentation, operational procedures and management are described for two watersheds used in a 2-1/2 year study of movement and losses of pesticides and nutrients from non-point sources in the Great Lakes Basin. Observed patterns of runoff and sedimentation are described in relation to weather conditions at different seasons of the year.

An assessment is made of sources of variation in pesticide analyses for soil cores taken during the period May 1973 through September 1974. A number of relationships to methodology, chemical species, topography, soil conditions and weather are identified:

a) Random variation is high and derives from variable distribution of chemicals during application, variability associated with sampling and analysis, and random patterns of pickup and interception from runoff.

b) Variation is present and can be interpreted in terms of movement downslope and within the plow layer, and in terms of loss by degradation and/or volatilization or by leaching out of the sampling zone into the subsoil.

c) Due to sampling bias, downslope movement within steeply sloping segments is reflected by increasing recovery, rather than by decreasing mass balances as might be expected. This relationship may change if the capacitances represented by depositional slopes and by retention in the plow layer are satisfied or exceeded by heavier rainfall in 1975.

d) Because of its resistance to degradation and its susceptibility to adsorption, paraquat was the most useful tracer for following movement and retention in the landscape. Losses by degradation or volatilization tended to mask the evidence for movement of other herbicides in this study.

e) Mobility (both downward in the profile and in surface runoff) was related directly to solubility: Paraquat > diphenamid > atrazine > trifluralin. The great mobility of paraquat was not expected and suggests interactions with fulvic acid components which inhibit its biological activity without immobilizing it.

f) Redistribution patterns reflected the effects of a number of factors on interception, infiltration and deep percolation of

rainfall and runoff. East-west (E-W) planter rows determined the direction of runoff from upper slopes, promoted cascading cross-row runoff in the central drainageway, and provided micro-relief for impoundment of runoff (with sorted sedimentation) at lower elevations. Granular structure of the plow layer on eroded slopes promoted infiltration and deep percolation of rainfall and runoff. Loosened structure and irregular surface of freshly tilled soil promoted interception and infiltration during earlier portions of each growing season. Length and pitch of slope were important, as well as exposure of slope to drifting snow and winter sun. The presence of a frost layer precluded deep percolation, promoted pickup of saturated soil materials on upper slopes and ponding at lower elevations. Lingering snow and ice promoted interception on intermediate slopes.

g) Differences between the two watersheds in distribution and retention of chemicals reflected mainly differences in length of E-W slopes and the proportion of gentle slopes where runoff flows tend to slow down or where ponding can occur. Soil differences were minor except in relation to topography and the degree of erosion and incorporation of granular subsoil materials into the plow layer.

h) Movement over the watersheds and through the soil was more rapid in summer 1974 than in 1973, reflecting rains of greater magnitude. In 1975, deeply penetrating rains and rains of erosive intensity were more frequent than in 1974. Greater downslope movement of chemicals may be expected because visible sediments were transported further down the drainageway in both watersheds. Corn and soybeans were much more vigorous in 1975, and differences between watersheds may reflect differences in nature of the canopy and its rate of development.

Weather and watershed conditions associated with runoff sequences during winter 1974-75 are described. Emphasis is placed on characterizing boundary conditions at the beginning of each event in relation to weather sequences which preceded it:

a) The depth and distribution of snow cover reflected effects of wind direction and local relief on patterns of drifting.

b) The depth, age and distribution of snow cover over the watersheds served to moderate the rates of penetration and disappearance of frost in the profile. Direction of slope, in relation to angle of insolation during the warmer part of the day, was an important factor affecting depth and quality of snow cover and disappearance of surface ice and of frost within the profile.

c) Snow, particularly new snow, can intercept rain and runoff and can delay net runoff from a watershed.

d) Frost in the profile prevents deep percolation of melt water

or rain and permits runoff from minor amounts of precipitation.

e) When surface soil thaws on warm or sunny days, it tends to remain saturated and soil particles are readily suspended in runoff. Upper slopes can drain quickly by seepage as soon as sources of melt water disappear.

f) Nightly freezing forms ice in saturated soil on slopes fed by seepage from above and in areas where ponding occurs during the day. This ice layer is slow to thaw, protects soil on slopes from erosion, but serves to intercept seepage on slopes and to seal the surface in areas of ponding. Under these conditions, seepage from thawed and saturated soil over frost in sloping areas can extend runoff for a time after rain stops or after sources of melt water have disappeared.

g) Sediment pickup from frozen soil is low, but sediment loads in runoff increase as the area exposed to thawing and saturation of surface layers increases.

h) The recharge capacity of thawed soil increases as deep frost layers recede. The quantity of precipitation needed to produce runoff increases accordingly.

i) Sediment yields in runoff collected at catchments provide a basis for identifying events and watershed conditions which produced major redistributions of sediments and chemicals within the watersheds.

Runoff data for major historic events in April and August 1975 are used to illustrate effects of crop cover per se and of crop characteristics (brace roots of corn, lodging of soybeans) on runoff volumes, sediment yields and losses of chemicals.

CONCLUSIONS

1. Weather sequences which precede a runoff event can influence, sometimes determine, the ratio of runoff to infiltration and percolation. During the early growing season, even light rains can modify surface structure and micro-relief, left by tillage, in ways which favor runoff. During colder seasons of the year, precipitation over a period of days or weeks can accumulate as snow which can be cumulatively effective as current precipitation when it thaws. The distribution of snow over the landscape can vary dramatically with drifting which, in turn, is influenced by wind velocity and by wind direction in relation to local relief.

2. When winter thaws occur in the Great Lakes Basin, with or without rain, infiltration and deep percolation are frequently controlled by the distribution of surface ice or of frost within the profile. The distribution of surface ice and frost are influenced by topographical features which determine insolation angle and patterns of down-slope seepage during periods

of daily thawing and nightly freezing.

3. Patterns of sedimentation which can be observed visually are not reliable for inferring patterns of redistribution of chemicals carried in runoff. Visible sediments represent coarser, heavier, less adsorptive soil fractions. Chemicals in solution or associated with very fine suspended matter may be intercepted at any point where infiltration of runoff occurs. Infiltration of runoff is promoted where runoff is slowed down on gentling slopes or by lingering snow or ice and, in particular, where ponding occurs.

4. The micro-relief afforded by planter rows and the impedance afforded by plant roots and stubble tend to control the direction of runoff on short slopes and contribute to the impoundment capacity in level basin areas. They also provide the conditions for cascading runoff and severe erosion on sloping areas which transect crop rows. Contour planting, no-till and good soil conservation practices would appear to be most important for controlling pollution from non-point sources in agricultural landscapes where cultivated crops must be grown.

5. The mobility of pesticides in soil and over the landscape appears to be primarily a function of their solubility and the degree to which they are adsorbed on suspended sediments. On the permeable soils of these watersheds, net losses from surface applications appeared to be minimal in relation to quantities retained by displacement into the plow layer and subsoil. In the case of less persistent chemicals, net losses in runoff were further reduced by volatilization and/or degradation.

6. In spite of its cationic character, paraquat was the most mobile of the chemicals in this study. It is likely that its displacement into the profile would have been less rapid on finer textured soils with higher exchange capacity. However, it is possible that its high mobility (which does correspond to its high solubility) was promoted by interaction with soluble, macromolecular components of the fulvic acid fraction of soil organic matter. Certainly, its phytotoxicity is destroyed by contact with the soil. If it does move in complexes that inhibit its biological activity, its appearance in runoff should pose no threat to natural systems in receiving waters.

SECTION II

RECOMMENDATIONS

1. Sampling segments as delineated for these watersheds failed to differentiate intermediate slopes where significant interception of runoff and dissolved or suspended chemicals occurred with little or no visible sedimentation. Each of the segments with major E-W slopes (01, 03, 04, and 06 in Fig. 8) should have been divided along contours into at least two smaller segments. This should be considered in any future studies on these watersheds. The principle applies to other watersheds as well.

2. Weather sequences which precede a runoff event can influence boundary conditions dramatically, notably during winter months. Important boundary conditions not characterized in this study, or for which only qualitative observations were made, include soil moisture content and distribution at the beginning of summer events, and the distribution of snow cover, surface ice and frost within the profile in relation to wind velocity, wind direction and angle of insolation during winter months as influenced by local relief within and around the watersheds. Costs for obtaining appropriately objective and detailed data on these parameters will be high but should be considered in any projections for developing second generation models for non-point sources of pollution under conditions in the Great Lakes Basin.

3. Losses of pesticide could have been reduced substantially by sound conservation practices such as contour planting, grassed waterways and winter cover crops. But losses in runoff from these watersheds were very low except for a major historic event in April 1975 in which 30 to 60% of the total loss occurred. Much of the loss during this event can be ascribed to sediments picked up from deep rills and gulleys cut along central drainageways by cascading runoff across rows of crop stubble.

SECTION III

INTRODUCTION

The challenge for the modern agriculturalist is to optimize food production generating the highest quality of food and fiber with respect to productivity, environmental quality and other national goals. This is necessary to feed an ever increasing population at an economical cost and without degrading the environment. The use of pesticides and fertilizers, i.e., agricultural chemicals, is a part of modern agriculture to meet the need for food production.

The necessity of using both fertilizers and pesticides cannot be questioned, but the need for careful evaluation of the fate of these materials once applied to farm land cannot be underestimated. Once applied to land, a pesticide may (1) be adsorbed by soil particles and either retained in the soil or move with the soil particles in the event of erosion, (2) remain in the water fraction of the soil and be subjected to leaching downward or to loss in surface runoff, (3) be vaporized into the air, (4) be absorbed by a crop and thus added to our food chain, or (5) be degraded by microbial, chemical, and photochemical processes in soils. The ultimate fate of an applied pesticide is then dependent upon (1) properties of the pesticide, (2) soil properties that affect the distribution of the pesticide between solid and liquid phases in the soil, (3) climate within a particular region which influences the quantity of runoff from a watershed, (4) management practices, and (5) watershed characteristics.

Many pesticides have been marketed in the past; undoubtedly, many more will be cleared by regulatory agencies for use in the future. The chemical properties of these pesticides may vary widely. To evaluate the runoff loss potential of each new pesticide by field experimentation would not be feasible from the view of either time or money. And many valuable years' use of a potentially useful pesticide would be lost by holding the material from the market until field experiments could be conducted. It is, therefore, important to seek ways of evaluating the erosion and leaching hazard of new pesticides by methods that do not require costly field experimentation for each individual chemical. The development of models for pesticide transport in field situations appears to offer a viable alternative for predicting pesticide loss. These models can then be validated with field data for carefully selected " model" pesticides and field locations.

The inclusion of watersheds from the Great Lakes Region in such a modeling program is important because the soil types are considerably different from Central, Southern, or Western United States; the climate includes snowfall leading to runoff and erosion from snowmelt during winter and spring. Two small watersheds existed on the campus farms at Michigan State University

which had been studied for many years prior to establishing the experiments described in this report. Their inclusion in this study was desirable because their history was known, weather records for about 35 years were available for the site, a small weather station was located adjacent to the watersheds for collection of weather data, and a portion of the physical structure necessary for these experiments was already on site.

The objectives of the project were to

1. evaluate the movement of several herbicides (differing widely in volatility, solubility, and susceptibility to adsorption) in the water and sediment being lost from agricultural watersheds in the Great Lakes Basin;

2. furnish Athens Environmental Research Laboratory, EPA, with analytical data and historical hydrologic and climatic data which will allow for evaluation, by systems analysis, of movement of pesticides in soils and agricultural landscapes;

3. describe modes of pesticide transport quantitatively in an agricultural landscape.

4. determine the effect of soil factors and micro relief on distribution and transport of pesticides from an agricultural watershed.

SECTION IV

EXPERIMENTAL METHODS

DESCRIPTION OF WATERSHEDS

Soil types typical of the Great Lakes Basin are found in two watersheds on the soil science farm at Michigan State University. The east watershed (hereafter referred to as 06) contains 0.80 hectare and the west watershed (hereafter referred to as 07) contains 0.55 hectare. The principal soil type of the watersheds is a Spinks loamy fine sand (figure 1). Watershed 07 contains some Tuscola fine sandy loam in the northwest corner. The slopes in the eastern 1/3 of watershed 06 are classified as Hillsdale fine sandy loam. Depositional materials in the central confluence area of 06 are classified as Traverse fine sandy loam. Official descriptions for these soil series are attached in Appendix I.

A detailed topographical survey made in 1942 is presented in figure 2. Slopes vary from 2 to 4 percent in front of the catchments to 10 to 12 percent at certain points in the watersheds. Areas with slopes of 6 to 12 percent in figure 2 correspond to areas of class 2 erosion in figure 1. In areas of 8 to 12 percent slope, subsoil materials have been exposed. Due to their coarsely granular structure, these materials form drouthy seedbeds so that germination is frequently reduced or delayed and early growth of crops is delayed. On upper slopes, near the watershed perimeters, soil moisture reserves are quickly depleted, and crops develop symptoms of water stress more quickly at any time during the season than at contour elevations only a few feet lower downslope. A protective canopy develops more slowly on upper slopes and is less dense at maturity. As a result, soils are exposed for longer periods to the erosive action of heavy rains.

The runoff catchments were initially concrete, with water flow being measured by means of standard waterstage devices at the weirs.

The watersheds were in continuous corn for over ten years prior to initiation of this project. During this period they received, on the average, 3.37 Kg/ha of atrazine and heavy applications of complete fertilizer each year. Livestock manure was applied in 1970 at a rate of 40 metric tons per hectare.

DETAILS OF CONSTRUCTION AND OPERATION

The precatchments, catchment basins and weirs were lined with stainless steel (see figure 3a). Stainless steel, 1:100, Coshocton wheels were constructed and connected by a belt drive to two DC auto heater fan motors for

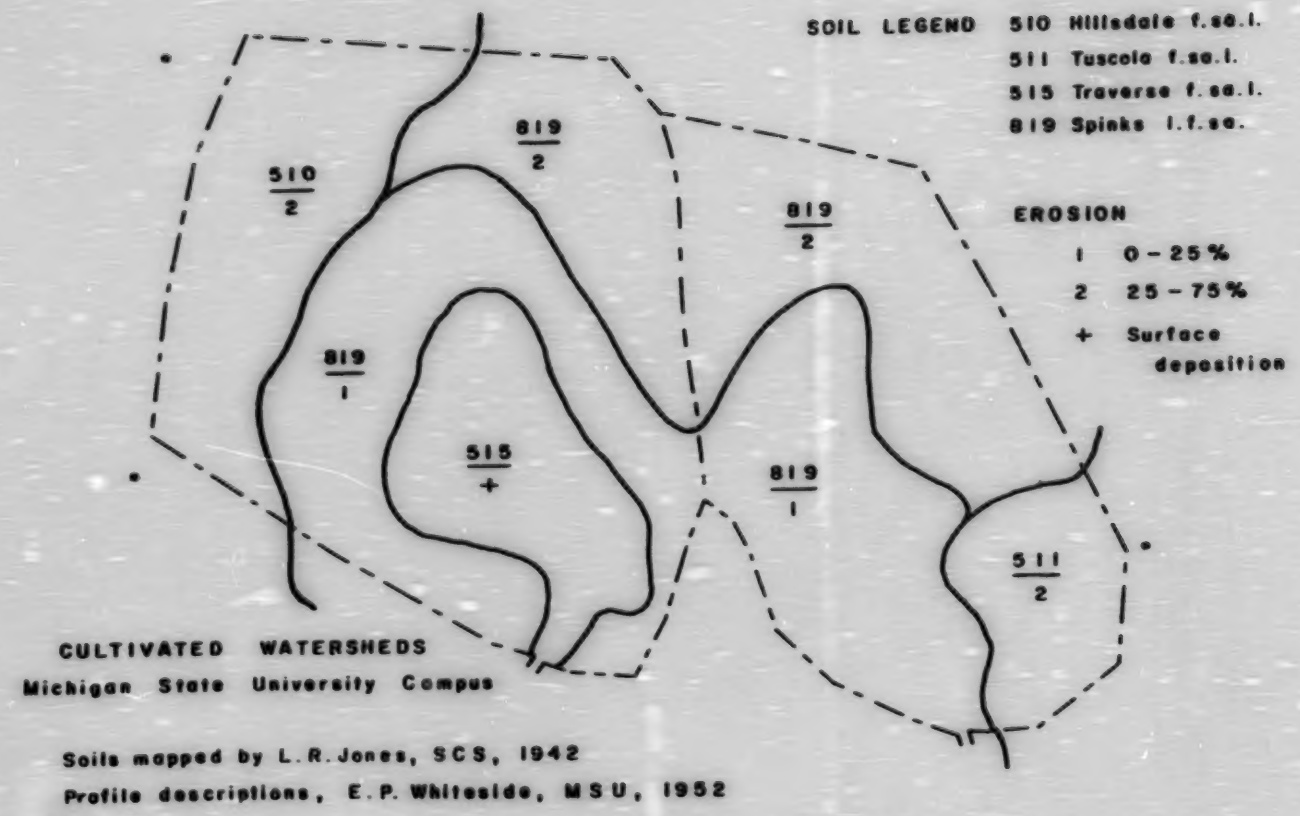

Figure 1. Principal soil types on the two watersheds (06 and 07) at Michigan State University farms.

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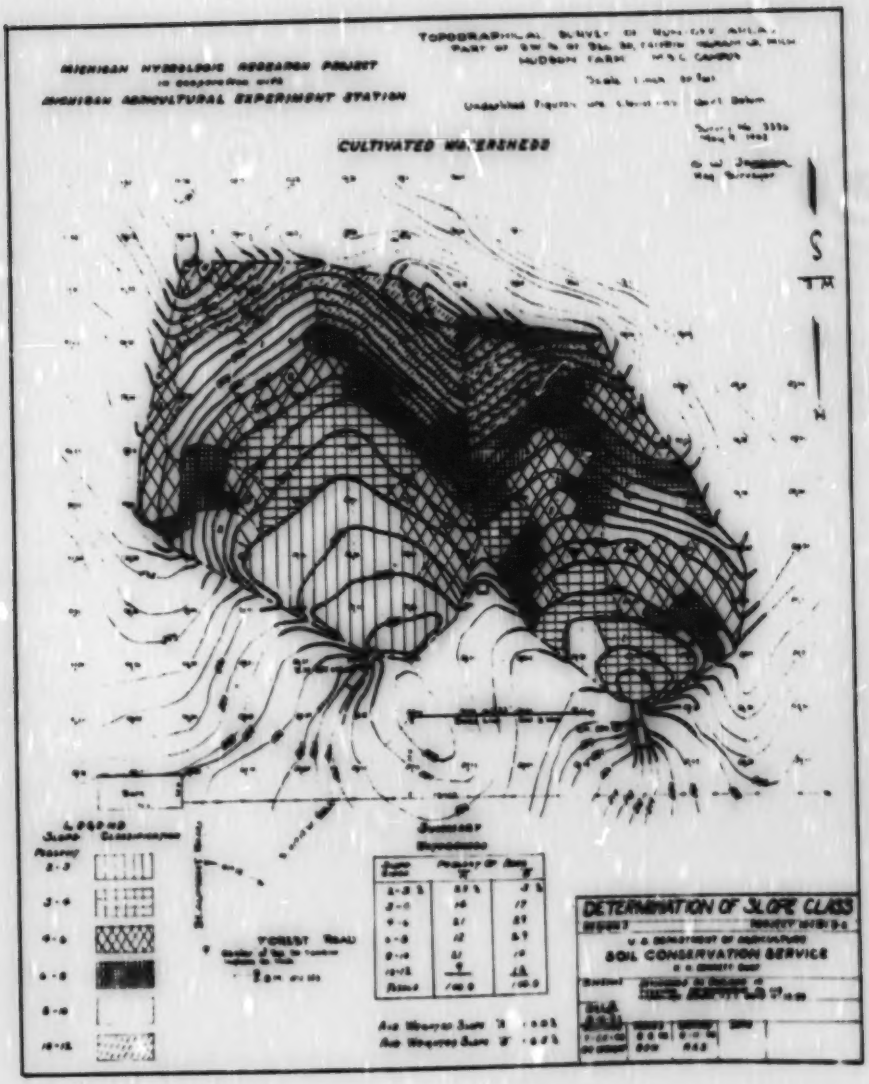


Fig. 2. Contours and slope classifications. MSU watersheds 06 and 07. (SCS 1942)

Figure 3a. Stainless steel linings of catchment basins (watershed 06).

Figure 3b. Stainless steel Coshocton wheel (watershed 06).

each wheel. One is shown in operation in figure 3b. Current was supplied by heavy duty storage batteries equipped with trickle chargers. A stainless steel pipe from the Coshocton wheel terminated in an optional (1:1 or 1:10) sample splitter prior to directing the samples to receiving containers on a rotating carrousel (see figure 4a). As shown in figure 4b, samples were collected in stainless steel pots. A float, attached to the delivery spout, was equipped with a mercury switch adjusted to close the circuit to the carrousel drive motor when one pot was full (about 10 liters) and open it again when an empty pot had advanced into place.

Heating tapes were installed below the stainless steel catchment liners and around the waterstage wells, delivery pipes and sample splitters to prevent those portions of the system from freezing during runoff periods in late fall to early spring. These were not always effective. In particular, the water in the waterstage well froze on several occasions, and two or three major winter runoffs were not registered. Runoff volumes for these events were calculated initially from collected sample volumes and nominal sample reduction settings. The originally reported waterstage records for these events have been adjusted for probably effective reductions calculated from computer output for other events when satisfactory waterstage records were obtained.

The Coshocton wheels and catchments were protected from direct precipitation by a corrugated steel roof. Plywood sides were installed around the front and sides of the catchments to reduce drifting of snow. A 5 cm gap was left at the lip of the catchment for runoff to enter, and on several occasions, southerly winds caused much more drifting inside the catchment through this gap than if the sides had not been present.

The Coshocton wheels were not protected around the sides. Frequently winter runoff under snow cover would continue for several hours after air temperatures had fallen below freezing with the result that Coshocton wheels and motors would be encased in ice, belts would break or pins would shear, and motors burn out. On several other occasions, snow drifted to depths of 1.8 to 2.4 meters over the Coshocton wheels and in the after-flume runoff channels. The snow was removed promptly from the Coshoctons and sample splitters, but on two occasions heavy runoffs occurred before the channels had been cleared to the outlet tile with the result that runoff backed up and overflowed through the sample splitter into the collection house. Fortunately, project personnel were on hand to open the channels before excessive overflow into the house had occurred. (A similar overflow situation developed during a torrential downpour on August 21, 1975.).

Buildings were constructed to enclose the instruments and carrousels. The collection houses were insulated and refrigeration units installed for keeping samples cool during the summer. Small space heaters had to be installed in winter to prevent water which entered by seepage or overflow from freezing and immobilizing the carrousels.

The paired fan motors used to drive the Coshoctons were normally adequate. During very heavy runoff events, they lacked power to drive the slot extension up into the flow of water. This contributed to erratic time intervals between samples and variable runoff flows for individual samples as calculated by the computer from recorded stage heights. Belt slippage may

Figure 4a. Stainless steel lead pipe and optional sample splitter (watershed 06).

Figure 4b. Stainless steel collection vessels in operation (watershed 06).

have contributed to this, but motors also heated excessively and, on several occasions, burned out during the event.

The motors for the Coshoctons were inexpensive, easily replaced, and spares were always kept on hand. To avoid excessive attrition, a rain pot with a water-contact switch was installed initially at each watershed to turn on the Coshocton wheel after 0.00039 cm of rainfall. This switch was replaced in April 1974 with a relay to the carrousel drive circuit. This relay activated the Coshocton motors after the first pot had filled.

The normal standby position for the Coshocton was with the slot centered under the lip of the flume (1/5 reduction). The sample splitter was usually set for a 1/10 reduction. Thus, the nominal reduction for the first sample of an event was usually 1/50. With the Coshocton turning (1/100 reduction), the nominal reduction for pots after the first one was usually 1/1000. On occasion the Coshocton cover was removed, giving only the 1/10 reduction at the splitter, or the sample splitter was sometimes opened so the nominal reduction was that for the Coshocton (1/100).

These reduction settings were recorded in the log for each event, but it was observed that effective reductions could vary widely from the nominal setting. During light runoff, the stream coming from the lip of the flume could meander from one side to the other so that all of it or none of it might enter the slot of the Coshocton. At any time, debris could lodge against the sample splitter and change the split materially. In the case of major events, pots were sometimes composited or some proportion discarded in sequence in the field, or the collected samples were composited in the lab or alternate samples discarded to reduce the numbers of samples for analysis. The disposition of each pot was recorded, and this has helped resolve many of the apparent discrepancies in computer output between runoff flows calculated from stage heights and flows expected from the numbers of samples reported.

During the first few events of 1973, sample collection times were recorded by project personnel. Rainfall times were also based on observation plus U. S. Weather (US WB) Bureau instruments and records for the official USWB reporting station which is located at the watershed site. Beginning August, 1973, rainfall times and sample collection times were recorded automatically on the same time scale with a 10-pen event recorder connected by relays to a tipping bucket rain gauge, to the Coshocton wheel motor circuits, and to the carrousel drive motor circuits.

Attempts were made to record waterstage heights on the event recorder also, but the waterstage recorders were disabled by the various hook-ups that were tried. Thus, our reported waterstage records for each watershed are based on clock times that are independent of each other and of the times reported for samples and rainfall.

Every effort was made to keep the three clocks synchronized and to log discrepancies when noted. Nevertheless, time discrepancies for numerous

events became apparent in computer output received from AERL. These have been reconciled by detailed examination of recorder charts and field logs to give what we consider to be a realistic record of these events as we experienced them. The time discrepancies would have been virtually impossible to detect without the parallel time frames supplied by the computer.

In spite of the operational difficulties noted, with a few noted exceptions, the data reported under this and the nutrient project is valid. Many of our difficulties probably are not unique. Some of those encountered during winter operations may be useful in design of similar facilities for winter runoff studies in northerly areas.

SOIL SAMPLE COLLECTION

Soil residue data reported for the summer 1973 and the winter 1973-74 runoff seasons represent four sampling segments for each watershed. These are shown in figure 5. Their relation to soil types and erosion classes is shown in figure 6.

Questions arose regarding the possibility that watershed perimeters may have been altered by tillage practices and that slopes may have changed due to erosion since the original topographical survey in 1942. Also, it was apparent that significant slope and soil differences could not be adequately represented by only four sampling segments.

The watersheds were surveyed again in May 1974. The contours obtained (figure 7) correspond well with those in the original survey (figure 2) except near the perimeters where tillage and erosion had softened the sharp ridges indicated in the earlier survey. By plowing and discing, a sharp berm was formed along the original perimeters and seeded to bromegrass just before the 1974 crops were planted. Breaks in the berm, resulting from harvest operations in the fall, were repaired again before planting in 1975.

At the time of the 1974 survey six sampling segments were delineated and their areas determined. These are shown in relation to contours in figure 7 and in relation to soils and erosion classes in figure 8. These segments did correspond well with observed patterns of wash-off, rill formation, and sedimentation.

Except for pre-treatment and mass balance samplings in the spring of 1973, soils were sampled to a depth of 30 cm (or to the depth of water penetration in dry soil). Seven depth increments were normally taken: 0 to 1 cm, 1 to 2.5 cm, 2.5 to 5 cm, 5 to 7.5 cm, 7.5 to 15 cm, 15 to 22.5 cm, and 22.5 to 30 cm. Ten to 15 cores were composited for each sampling segment (a larger number of cores was needed for the 1 cm and 1.5 cm increments to provide sufficient sample for both herbicide and nutrient analyses).

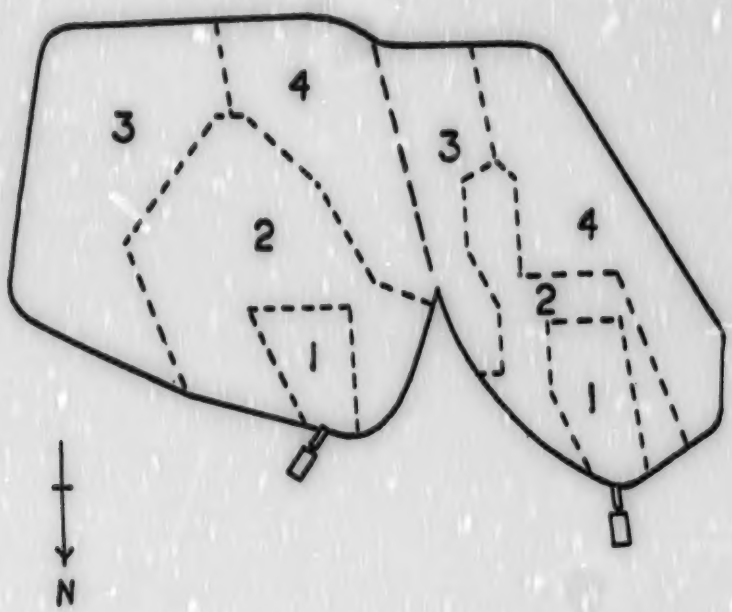
Numerous sampling devices were tried during the summer of 1973. A shielded, stainless steel sampling probe (approximately 4 cm I.D.) was developed which worked well after freshly tilled soil had settled. It was not satisfactory for sampling loose or dry soil, and the volume obtained from

East Watershed (006)

Segment	Acres
1	.14
2	.70
3	.61
4	.54
Total	1.98

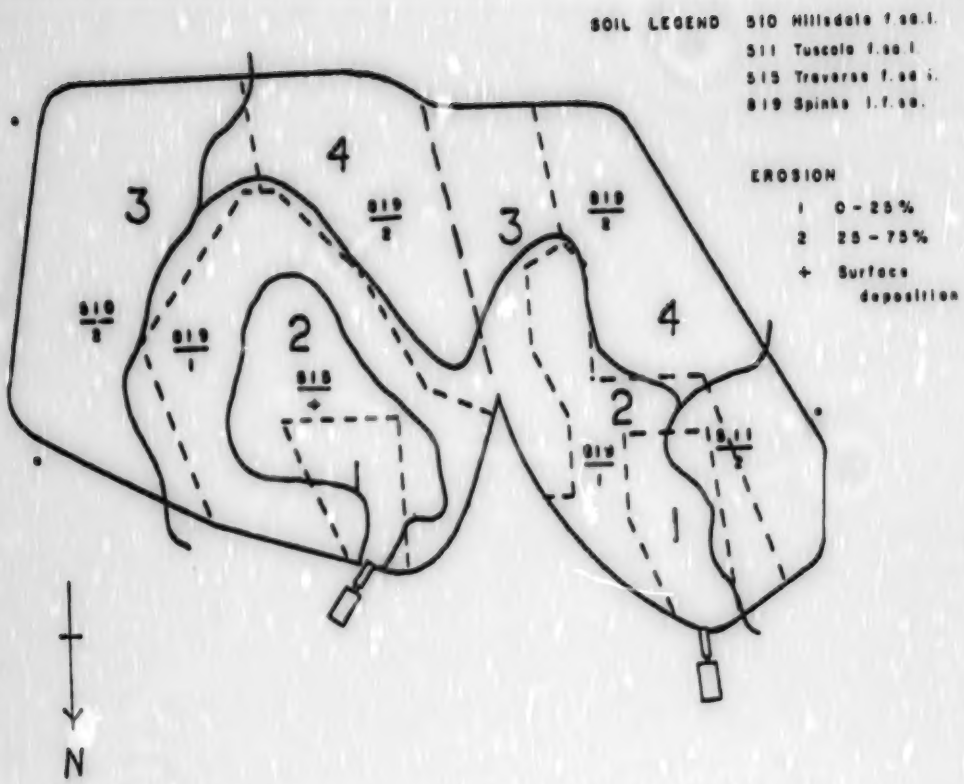
West Watershed (007)

Segment	Acres
1	.18
2	.36
3	.27
4	.54
Total	1.35



MSU WATERSHEDS

Figure 5. Sampling Segments 1973 - 74



MSU WATERSHEDS

Figure 6. Sampling Segments 1973 - 74 (With soils overlay)

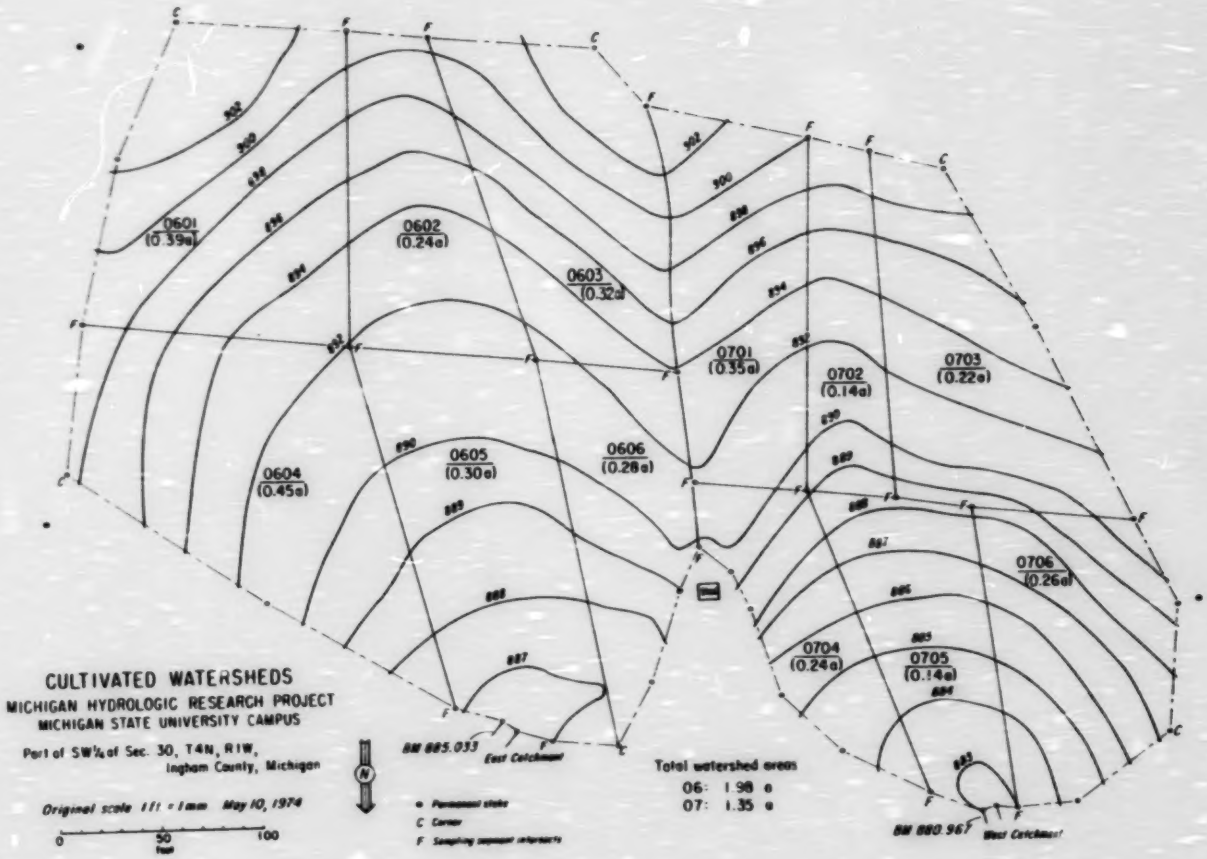


Figure 7. Sampling Segments 1974 - 75 (With topographic overlay)

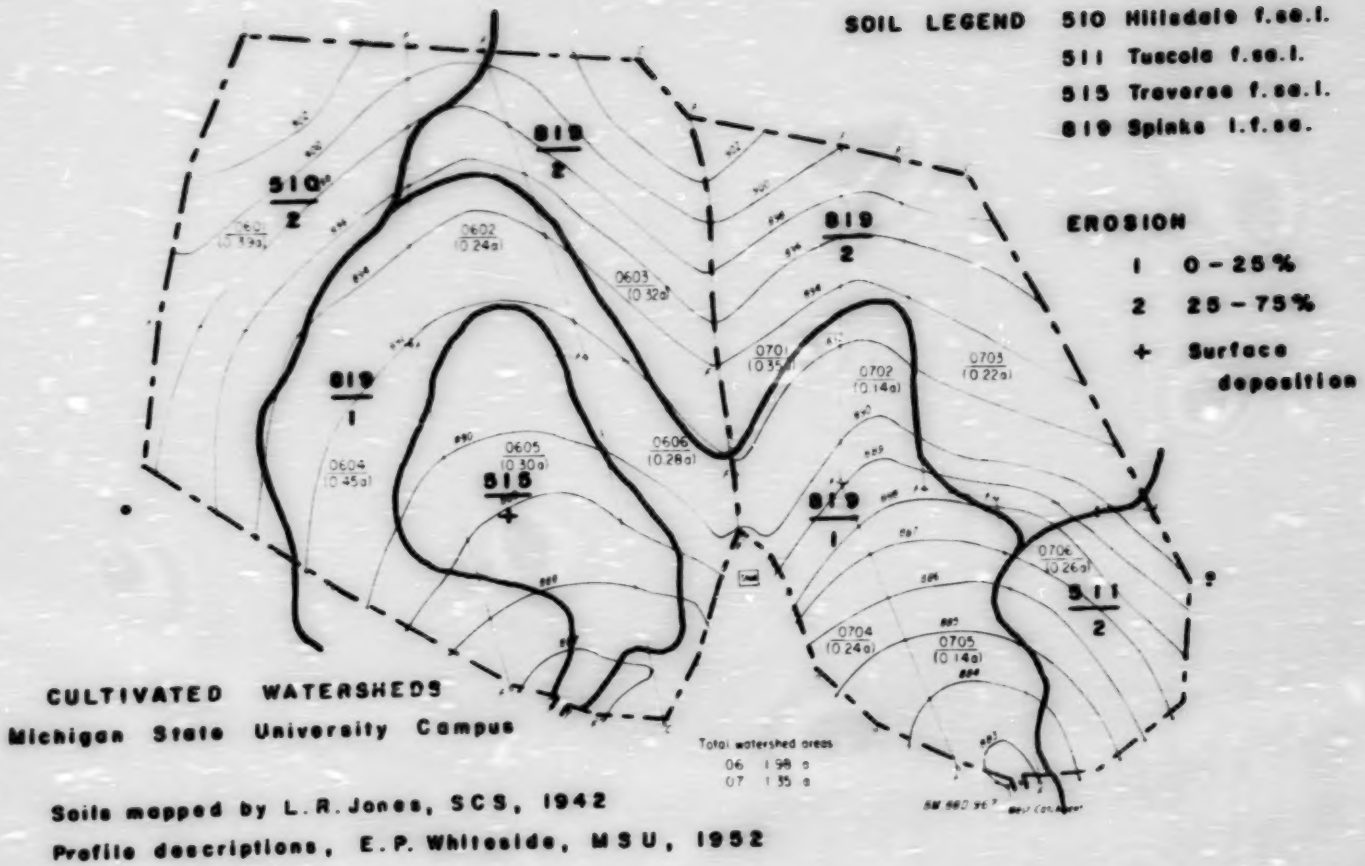


Figure 8. Sampling Segments 1974 - 75 (With soil and topographic overlays)

10 cores for the 1 cm and 1.5 cm increments did not supply the sample needed for all analyses.

A series of stainless steel "cookie cutters" was designed for sampling the 1, 1.5, and 2.5 cm increments. Large stainless steel spatulas (7.6 by 30 cm) were inserted into the soil to form a 3-sided frame from which the "cookie sections" could be taken with minimal contamination, even in dry, loose soil.

Several special samplings were made with these sampling tools to derive standard bulk density values for mass calculations.

RUNOFF SAMPLES

Each sample (approximately 3.6 liters) was passed through a stainless steel three-way splitter. One fraction was used for pesticide analysis,one for sediment analysis, and the remaining one for nutrient analysis.

The water and sediment phases were separated by passing each sample through a 0.45 u millipore filter for nutrients or a Whatman 42 filter for pesticides--the sample being retained on the filter is hereafter referred to as sediment, and that passing the filter is hereafter called water.

RESIDUE ANALYSIS

The analyses for paraquat, diphenamid, atrazine, and treflan (See appendix table 1) were done in accordance with methods published by EPA workers (Payne et al., 1974, Pope and Benner, 1974). Special instrumentation, methods, and parameters are noted below.

1. Paraquat was analyzed by scanning between 370-470 nm and measuring the maximum peak height (above baseline) at ~394 nm on a Beckman DBG spectrometer using 4 cm cells. When sediment samples were less than 1 gram, sufficient adjacent samples in time sequence were combined, where possible, before the acid digestion step and average values reported. Blind spike samples were run periodically to ensure uniformity among workers. The minimum detectable amount was 100 ng.

2. Atrazine, diphenamid and treflan were analyzed on a Beckman GC-4 adapted with a Coulson electrolytic conductivity detector operating in the nitrogen mode. The column oven temperature was set at 205° C for atrazine or trifluralin and 220° for diphenamid. The injection port was set to 270° C and the furnace was held at 850° C.

   Minimum detectable amounts (signal/noise =5) were 5 ng for

atrazine and treflan and 30 ng for diphenamid. It should be noted that soil samples were deactivated by equilibrating with water before extracting for these three chemicals.

When sediment samples were less than 1 gram, sufficient adjacent samples were combined, where possible, before G.C. analysis and average values reported. Blind spike samples were run periodically to ensure uniformity among workers. Mean recoveries from spiked samples are given in Table 1.

G.C. signals were fed to PDP-8/e computer via an AFC-8 A/D interface. PAMILA^{R} software permitted the computation of the data to peak area, height and retention times numbers which in turn were fed to a PDP-11/40-RSTS computer for storage and subsequent manipulation for report generation.

TABLE 1. RECOVERY OF CHEMICALS FROM SPIKED SAMPLES.

Chemical	Added	Recovered	Added	Recovered
	ppb	%	ppb	%
A. Spiked soil samples				
Atrazine	20	85± 5	100	86± 5
Diphenamid	100	82± 6	500	89± 5
Paraquat	300	90± 5	1,500	91± 4
Trifluralin	1,000	104± 3	2,000	89± 4
B. Spiked water samples				
Atrazine	1	85± 5	5	90± 4
Diphenamid	1	80± 5	5	88± 5
Paraquat	100	84± 6	500	85± 6
Trifluralin	1,000	98± 10	2,000	97± 10
C. Spiked sediment samples				
Atrazine	20	80± 7	100	90± 5
Diphenamid	100	80± 8	500	92± 5
Paraquat	300	90± 3	1,500	92± 2
Trifluralin	†		†	

† No estimates of recovery from spiked sediment samples were made for trifluralin.

SECTION V

RESULTS AND DISCUSSION

INTRODUCTION

The principal objective of this project was to furnish Athens Environmental Research Laboratory, EPA, with data which will allow the evaluation by systems analysis of movement of pesticides in soils and agricultural landscapes. In that the data from Michigan State University is only a portion of the data input, this section will deal principally with observations that are necessary to relate our data to soils and topography on the two water sheds and to weather conditions during the period of the study. Detailed discussion and conclusions that may ultimately be drawn from the data will not be covered in this final report.

A list of the field operations for each watershed is presented in table 2. Data from the study has been submitted at various times. A key to reports where the data from this study can be found is given below.

First year Summary, June 1973 to May 1974

Rainfall records	06-16-73 to 05-16-74
Runoff records	06-16-73 to 05-16-74
Pesticide residue data	06-16-73 to 05-16-74
Soil core data	05-24-73 to 05-02-74

Quarterly Report, May 1974 to September 1974

Rainfall records	05-17-74 to 08-31-74
Runoff records	05-17-74 to 08-27-74

Quarterly Report, October 1974 to December 1974

Rainfall records	09-02-74 to 11-28-74
Runoff records	09-12-74 to 11-05-74
Pesticide residue data	07-02-74 to 09-12-74
Soil core data	05-22-74 to 09-03-74

Quarterly Report, January 1975 to March 1975

Monthly USWB reports May 1973 to March 1975

Table 2. LIST OF FIELD OPERATIONS FOR WATERSHEDS 06 AND 07.

Date	Field Operation	Comment
05-24-73	Pre-experiment soil samples collected from 0 to 7.5 cm	Soil Sampling probe was used with 10 cores per sample
06-01-73	Watersheds plowed to 25 cm depth.	1972 crop was corn
06-05-73	Harrowed with spring tooth to smooth.	
06-07-73	Harrowed prior to broadcasting KCl.	Rate was
06-08-73	Trifluralin applied on both watersheds (06 and 07)	1.12 Kg/ha active in 215 liters per ha at 2.82 kg/cm^2 pressure applied between 0945 and 1045.
	Tilled with Tillivator (horizontal agitator) to a depth of 7.6 cm	Immediately following spraying to mix trifluralin with soil.
	Soil samples collected from 0 to 7.6 cm	Soil sampling probe was used with 10 cores per plot.
	Soybeans (var. Hark) were planted on both watersheds.	67 Kg/ha seed were used in 107 cm rows with 224 kg/ha of 12-12-12 placed 3.8 cm to the side and 3.8 cm below the seed.
06-09-73	Diphenamid (Upjohn 50% WP) and paraquat (Chevron 29.1% liquid, .24 Kg/liter were sprayed on both 06 and 07 in 430 liters/ha mixed slurry at 2.82 Kg/cm^2 to give 3.37 Kg/ha diphenamid and 1.12 Kg/ha paraquat.	Application was made between 0715 and 0850 hours.
	Soil samples collected from 0 to 7.6 cm at 4 increments of depth.	Surface soil was very dry and loose (bulk density 1.10± .10). It was moderately windy.

Table 2. Con't.

Date	Field Operation	Comment
06-08-73 to 06-11-73	Soil Samples collected for diffusion/ volatility studies.	
06-18-73	Soils sampled after runoff events	Soil sampling probe was used with 10 cores per sample, 4 increments to 7.5 cm.
07-04-73	Soils sampled after runoff events	Soil sampling probe was used with 10 cores per sample, 4 increments to 7.5 cm.
08-11-73	Soils sampled after runoff events	Soil sampling probe was used with 10 cores per sample, 7 increments to 30 cm.
10-11-73 to 10-15-73	Soybeans were harvested, and straw removed	Yield of 1,270 Kg/ha was obtained.
11-05-73	Diphenamid (Upjohn 50% WP) and paraquat (Chevron 29.1% liquid, 0.24 Kg/liter active) were applied on both 06 & 07 watersheds in a mixed slurry at 397 l/ha at 2.82 Kg/cm^2.	Application was made on frozen ground between 0900 and 1030 hours.
	Initial mass balance soil samples were taken in P.M. after soil has thawed.	Soil sampling probe was used with 10 cores per sample, 7 increments to 30 cm.
03-05-74	Soil samples collected.	
05-02-74	Terminal mass balance soil samples were collected.	

Table 2. Con't.

Date	Field Operation	Comment
05-20-74	Basic fertilizer applied and tilled in to a 7.5 cm depth.	57 Kg/ha N, 77 Kg/ha P and 144 Kg/ha K were applied.
05-21-74	Watershed 06 planted to corn (Pioneer 3780) and Watershed 07 planted to soybeans (Hark).	107 cm rows, 54,000 to 59,000 seeds per ha for each crop.
05-22-74	Paraquat (1.12 Kg/ha active) and atrazine (at 4.49 Kg/ha active) were applied to Watershed 06.	No spreader was used with paraquat. Applied between 0745 and 1030
	Diphenamid at 3.37 Kg/ha active) and paraquat (1.12 Kg/ha active) were applied to watershed 07.	Applied between 0745 and 1030.
	Soil samples collected.	"Cookie cutters" were used for the increments to a depth of 7.5 cm. Soil probes were used from samples from 7.5 to 30 cm. Ten cores per sample were taken.
05-30-74	Soil samples were collected from both watersheds.	Collected as on 05-22-74.
07-03-74	Soil samples were collected from both watersheds.	Collected as on 5-22-74
08-05-74	Soil samples were collected from both watersheds.	Collected as on 05-22-74.
08-14-74	Soil samples were collected from both watersheds.	Collected as on 05-22-74.

Table 2 Con't.

Date	Field Operation	Comment
09-27-74	Corn silage harvested from 06.	Yield was 27.8 metric tons/ha.
10-18-74	Soybeans harvested from 07.	Yield was 2,019 Kg/ha.
11-07-74	Fertilizers were broadcast at NH_4NO_3 & KCl.	Actual application was 130 Kg N/ha and 141 Kg Cl/ha.
11-08-74	Paraquat (1.35 Kg/ha active) and atrazine (2.69 Kg/ha active) applied to 06.	
	Diphenamid (at 3.7 Kg/ha active) and paraquat (1.23 Kg/ha active) applied to 07.	
	Soil samples collected.	Collected as on 5-22-74.
11-22-74	Soil samples collected for bulk density analysis.	
02-03-75	Soil samples collected.	0 to 1 cm sampled.
05--8-75	Soil samples collected for terminal mass balance.	Collected as on 05-22-74.
05-16-75	Watersheds were plowed.	
05-16-75	Fertilizers were broadcast as NH_4NO_3, $Ca(H_2PO_4)$ and KCl and worked in to a depth of 7.5 cm with a tillivator.	Applied 68 Kg N/ha, 131 Kg P/ha, 172 Kg K/ha and 156 Kg Cl/ha.
	Watershed 06 planted to corn and Watershed 07 planted to soybeans.	107 cm rows, 54,000 to 59,000 seeds per ha for each crop.

Table 2. Con't.

Date	Field Operation	Comment
05-17-75	Paraquat (1.28 Kg/ha active) and atrazine (2.56 Kg/ha active) applied to 06.	
	Diphenamid (at 3.12 Kg/ha active) and paraquat (1.03 Kg/ha active) applied to 07.	
	Soil samples collected for beginning balance.	Collected as on 05-22-74.
06-02-75	Soil samples collected after runoff.	Collected as on 05-22-74.
06-06-75	Soil samples collected after runoff.	Collected as on 05-22-74.
06-20-75	Soil samples collected after runoff.	Collected as on 05-22-74.
06-25-75	Corn sidedresses with NH_4NO_3.	64 Kg N/ha.
07-21-75	Soil samples collected after runoff.	Collected as on 05-22-74.
08-12-75	Soil samples collected after runoff.	Collected as on 05-22-74.
08-27-75	Soil samples collected for terminal mass balance.	Collected as on 05-22-74.

Quarterly Report, April 1975 to June 1975

Rainfall records	12-01-74 to 05-30-75
Runoff records	01-08-75 to 05-30-75
Monthly USWB reports April and May 1975	
Soil core data	11-08-74 and 02-03-75

Quarterly Report, July 1975 to September 1975

Rainfall records	06-01-75 to 09-29-75
Runoff records	06-05-75 to 08-31-75
Soil core data	05-08-75 to 06-02-75
Monthly USWB reports June 1975 to September 1975	

Special Report, December 22, 1975

Pesticide residue data	01-08-75 to 08-22-75
Soil core data	06-06-75 to 08-27-75

Special Memo, February 1976

Discrepancies in first computer printout for period 06-03-73 to 11-28-74.

Special Report, September 1976

Field Notes on Crop Development: 1973, 1974, 1975.

Special Memo, October 1976

Reconciliation of computer printout received June 1976 with transmitted data and all available records and field logs.

In this section we have two objectives: (1) to describe soil conditions, topographical features, and patterns of runoff and sedimentation which would have influenced profile distributions and mass balances within sampling segments and lateral redistribution from one segment to another; (2) to describe weather and watershed conditions associated with a sequence of winter runoff events in 1975 and with two major historic events in spring and summer 1975 (one without crop cover and one with mature crop cover).

Rationale will be presented for resolving some of the apparent anomalies in our soil core data for pesticides through September 1974. Corrected runoff data will be used to show effects of freezing and thawing on winter runoff losses and to show unique differences between the two watersheds in their susceptibility to losses of sediments and chemicals.

Runoff and Sedimentation Patterns

The two watersheds differ in size and are uniquely different in topography (Fig. 2). Soil differences (Fig. 1) are minor except as they relate to topography. The Tuscola fine sandy loam in the NW corner of Watershed 06

was developed in somewhat finer parent materials than the Spinks, as was the large area of Hillsdale on the east side of Watershed 06. However, subsoil materials exposed on 8-12% slopes of Hillsdale and Spinks are similar (cf. soil descriptions).

The large area of Traverse fine sandy loam in the central basin of Watershed 06 has no parallel in Watershed 07. The Traverse is a depositional soil, formed in sediments eroded from surrounding slopes. Sedimentation patterns observed in this area during the three growing seasons and two winter periods of this study will be described later in this subsection.

The plow layer in the more severely eroded areas of Spinks, Hillsdale and Tuscola (8-12% slopes) has a coarsely granular, open structure. Where freshly plowed, these slopes have a high infiltration capacity. Under rain action, infiltration is reduced by slaking at the surface and by the formation of a weak, thin crust (2 to 3 mm).

As observed in our core samples, the slaking action extended to a depth of about 2 cm. A single grain structure was found below the surface crust in our 0-1 cm depth increment. In the 1 - 2 1/2 cm increment, there was a gradation from fine to coarse aggregates. Below 2 1/2 cm, an open, porous structure was retained through the plow layer (25 cm) from one season to the next. Some consolidation did occur because, two to three weeks after plowing, probe sampling below 7 1/2 cm was virtually impossible unless the soil was moist.

Substrata below the plow layer in all areas drain freely, although local variations in deep drainage may occur due to discontinuous textural bands of finer materials. A 5 to 20 cm layer of silty clay loam is encountered at depths of 75 to 150 cm in and around the central ridge between the two watersheds (E. P. Whiteside, personal communication). Also, in the spring of the year, a perched water table approaches the surface at lower elevations near the catchments--a fact that was brought to our attention on 05-14-74 when the tractor nearly mired making the last two passes with the plow in front of the catchments.

The porous internal structure of the plow layer on eroded slopes, combined with freely draining substrata, would be conducive to downward displacement by sifting and percolation of fine materials released by slaking at the surface. We think that this explains, at least in part, the unexpected downward movement of paraquat in the profile, which is indicated by our data for segments which include severely eroded slopes (segments 3 and 4 in 1973, Fig. 6, and segments 01 and 03 in both watersheds, 04 in Watershed 06 and segment 06 in Watershed 07 in 1974 and 1975, Fig. 8).

Several light rains or a single rain of moderate intensity would serve to slake the soil surface and smooth irregularities left by tillage operations so that runoff from eroded slopes could occur readily. Even a light rain (5-minute intensity of 0.02 cm/hr) could produce runoff from upper slopes if it continued for several hours.

Frequently, rains of moderate intensity and short duration would produce

runoff from upper slopes, but sediments picked up on upper slopes would be intercepted on intermediate slopes before reaching the central draw or the gentle slopes of the central basin. During winter runoff events, lingering patches of snow on intermediate slopes were most effective in intercepting sediments from runoff water seeping through them or spreading laterally to flow around them.

Evidence of sedimentation on intermediate slopes was quickly erased by later events so we discounted it in laying out our sampling segments. However, examination of our soil core data through September 1974 leads us to believe that substantial movement of sediment from upper to intermediate slopes did occur within sampling segments 3 and 4 in 1973 (Fig. 6) and within segments 01, 03, 04, and 06 in summer 1974 (Fig. 8). Random sampling within these segments would have weighted our composites unduly in favor of depositional intermediate slopes. As a result, our data show increasing total recoveries for these segments over time instead of decreases as would be expected. Depositional areas within these segments include eroded slopes with open, porous structure in the plow layer so that our sampling bias is reflected at depths greater than 7 1/2 cm as well as in the upper increments.

The apparent sampling bias in eroded segments was greater for paraquat than for other chemicals, as would be expected because of its greater persistence and its total affinity to the particulate phase. Total recoveries for both watersheds in 1974 exceeded the total applied. A similar result would be expected for phosphorus and should be looked for in our nutrient data.

To understand patterns of erosion and sedimentation on these watersheds, it must be recognized that crops were planted east and west, at approximately right angles to the major slope and central drainageway. As a result, even during the winter, runoff from upper slopes followed row middles east or west toward the central draw of each watershed.

Because of the short E-W slopes, erosion down crop rows was mainly sheet erosion. Only occasionally were small rills (5 to 8 cm deep) cut in the track left by the covering discs on the planter. The principal occasion when this occurred was during the heavy rains of 04-18-75 when ponded water outside the berm broke through at several points along the east side of watershed 06.

When row middles at upper elevations in the central draw filled to overflowing, cross-row rills would form quickly and produce a rapid cascading discharge onto more level areas down slope. Deep cuts (10 to 30 cm) could be produced very quickly. These might extend across ten or more rows before reaching a point where sufficient ponding in row middles could occur to slow the flow of water.

On slopes of 4% or less (Fig. 2), impounded water might spread several meters up and down the row before breaking through into the next row middle. At this point, a new deep rill or gully might form, or simply a succession of mid-row ponds connected by shallow rills cutting across the ridges left by the planter.

At points where discharge from a rill or gully entered an area of ponding, the heavier sediments would be dropped quickly. Conspicuous deposits of light-colored fine sand would be left, extending up and down the row and sometimes in two or three successive rows below the point of discharge. Near the extremities of these deposits the light-colored sands graded abruptly to darker colored, very fine materials which blended quickly with the soil so that the limits of their lateral or downslope distribution could not be ascertained.

Another important feature of cross-row erosion in central areas of both watersheds is that deep rills and gullies were quickly obstructed by debris intercepted by plant roots or stubble. During the course of a major event or during subsequent lesser events, even a deep gully extending through the plow layer could fill with sediment.

Sediments deposited in rills and gullies were mainly the heavier sand fractions. These were less susceptible to cutting than unsorted soil. Successive episodes of cutting would start at different points along the E-W axis and at different points along the S to N slope of the draw. The result was a random, meandering pattern of alternate cutting and filling along the central NW-SE axis of both watersheds.

Usually, rills would cut no deeper than 10 to 20 cm before filling again. However, during the near-record rains of 04-18-75 and 08-21-75, cutting at several points in both watersheds extended through the plow layer to depths greater than our 30 cm sampling. Gullies left open at the end of these events had not been filled by the time of our terminal mass balance samplings of 05-08-75 and 08-27-75. Those left in April were covered by plowing in May; those left in August had largely filled with sediments by harvest time in October.

Cross-row rills were not wide, usually no more than 10 or 15 cm. However, their meandering pattern and random distribution would have influenced depth distributions of herbicides and nutrients over significantly large central areas in both watersheds.

The sediments deposited in rills and gullies were mainly light-colored fine sand--in other words, the least adsorptive soil fractions. However, there were textural bands of dark-colored finer materials, varying in thickness or frequency, as well as occasional slumps of soil from the sides of the rill or gully.

The random distribution of cross-row rills and gullies and the stratified variability of sediments deposited in them must be considered in interpreting changes in profile distribution of chemicals and nutrients from one sampling to the next. In particular, some of the date-to-date variation below 7-1/2 cm may represent a random weighting of our composite samples by cores taken in sediments deposited in deep rills.

On the other hand, changes over time in the upper two or three sampling levels (depth increments) will be influenced by the sorting out of heavier sediments on the surface along lateral mid-row sedimentation fans at points

where cross-row rills discharged into areas of ponding. These light colored surface deposits were generally thin and limited in extent at the higher elevations corresponding to segments 0602 and 0702 in Fig. 8. Only limited ponding could occur in these areas because of the steep E-W slopes. In these areas, visible sedimentation was associated also with down-row runoff from east and west. Sediments from steep slopes in segments 01 and 03 contributed to rapid filling of cross-row rills and gulleys at these higher elevations in the central draw.

Opportunities for ponding increased markedly on slopes of 4% or less, beginning at about the 894 ft contour in watershed 06 and the 890 ft contour in 07 (Fig. 2). At lower elevations, patterns of cross-row cutting and lateral sedimentation were uniquely different on each watershed and varied from season to season.

In watershed 06, extensive ponding can occur in row middles on the large area of 2-3% slopes. Ponding was infrequent during summer 1973 and the following winter. Cross-row cutting at higher elevations was light also, and the heavier, light-colored sediments from these rills were deposited in a limited area along the central draw in segment 2 of Fig. 6. Meandering shallow rills were formed in Segment 1, but conspicuous sorting out of heavier sediments occurred in only a few rows and the lateral surface deposits were thin.

The following summer (1974), runoff flows were somewhat heavier, cutting was more extensive, and sorting of sediments was observed all the way to the catchment. At the time of the 09-03-74 mass balance sampling, surface deposits of light-colored materials were generally thin and scattered, but, at several points in segment 0605 (Fig. 8), they extended for several meters up and down the row and were 1 to 2 cm thick.

During winter runoff events, soils in the Great Lakes Basin which are not under vegetative cover are, nonetheless, very frequently protected against deep cutting by surface ice or by the presence of deep frost in the soil. On the other hand, pickup of sediments by running water is facilitated when bare soil on the immediate surface thaws, since internal drainage cannot occur into the frost layer below. The thawed soil tends to remain saturated and readily suspended.

In permeable soils on sloping areas, saturated soil over frost can drain quickly by lateral seepage as soon as snow to supply melt water disappears. Seepage from upper slopes serves to keep thawed soil further downslope saturated. During winter thaws, night temperatures usually fall below freezing, and thawed surface soil freezes each night. The ice which forms in saturated soil thaws less readily the next day. Over a succession of daily snow melts with nightly freezing, ice builds up on the soil surface. Soil on intermediate and lower slopes is protected, thereby, from significant erosion. Lower basin areas are effectively sealed so that any runoff from surrounding areas will accumulate on the surface. Overflow will occur as soon as the impoundment capacity of local micro-relief is exceeded.

Deep frost disappears more slowly in areas where surface icing has

occurred. Disappearance of ice and frost is affected further by lingering patches of snow. Disappearance of snow cover is influenced by patterns of drifting (as determined by wind direction and local relief) and by the mean angle of incidence of insolation (as determined by season and by direction of slope).

On these watersheds, snow disappeared first on upper slopes, next in lower basin areas, and last on the north-facing slopes. Surface ice and deep frost disappeared in the same order.

During winter runoff periods, overflow from lower basin areas in both watersheds was frequently impeded by drifted snow in front of the catchments, and extensive ponding occurred during the day. Meandering flows and sedimentation in these areas were influenced further by lingering patches of snow and by random patterns of disappearance of surface ice. In watershed 06, meandering was promoted also, as snow and ice disappeared, by the relative resistance to cutting afforded by sandy deposits left from summer events. An additional factor in sedimentation and leaching was the reestablishment of internal drainage as deep frost disappeared, beginning around the periphery and progressing in random fashion through areas subject to ponding.

By the time of the 04-18-75 event, sorted sedimentation patterns at points of rill discharge were scattered randomly in segment 0605 over an area approaching the extent and outline of the Traverse fine sandy loam. Visible deposits in the east and west thirds of this area were thin and not extensive. These peripheral deposits mingled frequently with similarly thin (2-3 mm) and non-extensive light-colored sediments originating in down-row runoff from segments 0604 and 0606.

The widely meandering rills cut during winter events were not deep. Deep cutting did occur during the event of 04-18-75. Major cuts (20 to 30 cm) occurred along the central draw, transecting sedimentation patterns laid down earlier. Nevertheless, considerable meandering occurred in areas of 2-3% slope. Rills formed in these level areas were of moderate depth (10-15 cm), and extensive sedimentation fans were formed. In several places, light-colored sand deposits, up to 5 cm deep, extended several meters east or west from points of rill discharge and across several rows of corn stubble.

After plowing and planting on May 16 and 17, 1975, new patterns of cutting and sedimentation were initiated quickly by frequent moderate to heavy rains beginning 05-21-75. Meandering along the central draw increased as the corn crop developed, particularly as brace roots were extended to obstruct cross-row flows, beginning early in July. Some moderately deep rills (10-15 cm) were cut during early events, mainly in segment 0602 (Fig. 8). Cutting became shallower as meandering increased. Sorted surface sediments in 0605 were generally thin, but by mid August their random distribution was as extensive as at the end of the previous winter.

As in the case of the 04-18-75 event, the very heavy rain of 08-21-75 produced deep rills and gullies which transected earlier sedimentation patterns. However, in the presence of a fully developed corn crop, meandering in areas of 2-3% slope was more extensive than in April, and a larger

proportion of the area was affected both by deep sedimentation in rills and gullies and by lateral surface deposits.

In contrast to 06, areas in watershed 07 where runoff down the central draw can spread laterally are limited to a rather narrow band of 3-4% slopes below the 890 ft contour (Fig. 2). The opportunity for ponding in row middles reaches its widest extent between the 888 and 885 ft contours. This area includes the wide portion of segment 2 in Fig. 6 and the south one-third of segment 1. Ponding below the 885 ft contour was variable because of the tendency, even during events of only moderate magnitude, for runoff flows to converge into one or two deeper rills which would drain the area quickly to the catchment.

Because of the limited impoundment capacity in watershed 07, rills cut in areas corresponding to segment 0705 in Fig. 8 were deeper than in 0605, meandering and lateral sedimentation were less extensive, surface deposits were thinner, and the heavier light-colored s[illegible]ents were carried further down the drainageway.

During summer 1973 and again during summer 1974, cutting and filling, together with sorted lateral sedimentation in row middles, was observed all the way to the catchment. During both winter runoff periods (1973-74 and 1974-75), sedimentation in the area below about the 884 ft contour (Fig. 2) was promoted by ponding due to drifted snow in front of the catchment.

During summer 1975, a number of events, beginning early in the season, were of sufficient magnitude that deep rills were cut which drained the areas below the 885 ft contour quickly before much ponding or lateral sedimentation could occur. Over a succession of events, rills would fill and new ones form, but meandering was narrowly restricted. Some lateral sedimentation did occur during lesser runoff events.

During the very heavy rains of 04-18 and 08-21-75, a central gully was scoured through the plow layer, beginning at about the 883 ft contour. A substratum of glacial outwash cobbles was exposed over areas up to a meter wide, and washing of the plow layer extended over a wider area.

Soybeans lodged extensively in central areas of segments 0702 and 0705 where deep cutting occurred on 08-21-75. The fallen vegetation served to slow runoff flows during later events and promote sedimentation. This is reflected in our runoff volumes and sediment yields for the event of the following day.

Some sedimentation in rills and gullies undoubtedly occurred during the event of 08-22-75. However, major cuts were still open at the time of our final mass balance sampling on 08-27-75. By harvest in October, most deep rills in segment 0702 and the upper half of 0705 had filled. Due to interception of sediments at higher elevations, not much sedimentation had occurred in the central gully below the 883 ft contour.

Another feature of difference between the two watersheds is that E-W slopes in segment 0706 and parts of 0704 (Fig. 8) were steeper than in the

corresponding segments of the other watershed. Sediments in down-row runoff from these areas were carried further into the central draw and contributed to visible surface deposits and to filling of cross-row rills in 0705. Because the slopes were short, the surface deposits were thin, however.

It is difficult to anticipate how the unique differences in patterns of erosion and sedimentation on the two watersheds during each runoff period will affect our soil core data. However, expected differences do appear in the runoff data.

Because of the very much larger area where ponding and sedimentation could occur in the central basin of 06, runoff which could be measured at the weir occurred less frequently, sediment yields were generally lower, and total sediment losses during major events were less than on 07. The larger sediment losses from 07 included a larger proportion of less adsorptive sand, and this is reflected in lower concentrations of paraquat in the sediment phase.

A further comment should be made regarding effects of freezing and thawing on patterns of sediment pick-up and resedimentation. Our observations in winter 1973-74 were rather superficial but consistent with more detailed observations in winter 1974-75.

Depth of freezing was related to slope and snow cover. Depending on wind direction, snow would drift on slopes facing NE or NW, leaving only 5 to 10 cm trapped by stubble on upper slopes and variable depths in central basins. During freezing cycles, frost would penetrate quickly and to great depths (45 cm) if the soil were bare. Under snow cover, the rate of frost penetration would be related inversely to the depth of snow. Once frozen, however, the soil would not begin to thaw until snow cover became thin and granular so that the sun's rays could penetrate. At that point, the surface centimeter or two would thaw quickly in bright sun even when air temperatures were at or slightly below freezing.

Soil thawing under departing snow cover is saturated with water that cannot be removed by percolation into frozen soil underneath. Soil materials are, therefore, readily picked up by moving water if snow melt is rapid and, in particular, if snow melt is accompanied by even a light rain. During periods of thawing in winter months, the soil usually freezes again at night. Alternate freezing and thawing serves to keep soil materials on the surface loose and readily suspended in moving water.

Because of the normally thinner snow cover on upper slopes and their more direct exposure to a southerly sun, the upper slopes experienced frequent cycles of freezing and thawing and were frequently bare of snow at the time of winter rains.

Very little movement of sediments was observed on these upper slopes resulting from snow melt alone. However, as snow cover disappeared from areas on intermediate and lower slopes surrounding the central basins, considerable pick-up and redeposition was observed, without rain, due to water flows originating in snowmelt and seepage from higher elevations. Patterns

of redeposition were influenced markedly by lingering patches of snow and/or ice.

In the central basins, lingering patches of snow increased the meandering of runoff flows. Thus, areas affected by alternate cutting and filling and lateral sedimentation increased markedly. For this reason, sediment yields in our data for winter events involving mainly snowmelt are low and do not reflect the extensive pick-up and redeposition of sediments that occurred within each watershed. On the other hand, winter events involving both snowmelt and rain usually produced sediment yields substantially higher than did rains of similar intensity or duration on unfrozen soil at other seasons of the year.

SOIL CORE DATA, MAY 1973 TO SEPTEMBER 1974

In tables 3 to 12, available computer summaries have been condensed to focus on changes in recovery of pesticides in surface soil layers (0 to 7-1/2 cm) and at greater depths (7-1/2 to 30 cm).

Sources of variation

Recoveries from spiked samples were reproducible (±5 to 12%) and ranged from 82 to 89% for atrazine and diphenamid and from 89 to 104% for paraquat and trifluralin (Table 1).

Recovery on filter paper monitoring discs in the field was more variable and appeared to have been influenced by slope, direction of movement of the sprayer, and by wind direction at the time of application. Variation among 10-disc means for upslope and downslope traverses and traverses on the level was ±18 - 19% of overall recovery for atrazine, ±22 - 35% for diphenamid, and ±8 - 19% for paraquat. Overall disc recoveries in the last three applications ranged from 54 to 112% of calculated tank delivery for atrazine, 67 to 79% for diphenamid and 71 to 141% for paraquat.

A disturbing feature is the very low recovery of all chemicals immediately after the first application in 1973 (Tables 3, 5, 7, 8, 9, 10). These low initial recoveries may reflect sampling difficulties. The weather was windy, the soil very dry and loose, and we were still experimenting with sampling devices.

After the initial sampling, recoveries of paraquat and trifluralin increased and the sums for both watersheds remained rather stable for 2 or 3 samplings (Tables 3 to 8). Total recoveries of diphenamid did not change materially over the first 3 or 4 samplings (Tables 9 and 10). Averaging the sums for 06-18 and 07-04-73, recoveries expressed as percent of applied (for 06 and 07 respectively) were: paraquat (73 and 95%), trifluralin (97 and 66%), and diphenamid (31 and 28%). These recoveries may be compared with mean recoveries from spiked samples: paraquat (90± 5%), trifluralin (97± 12%), diphenamid (86± 10%).

Soils are loose and rough at the surface after tillage operations, more conducive to infiltration than runoff. Hardly any net runoff occurred at the

TABLE 3. WATERSHED 06 PARAQUAT* MAY 1973 TO MAY 1974

Date	Depth cm	Grams paraquat remaining				Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Increment	0-30
05-24-73	0-7½	0	0	0	0	0	0
06-09-73	0-7½	25	81	82	140	328	
06-18-73	0-7½	43	287	186	137	652	
07-04-73	0-7½	36	213	203	216	668	
08-11-73	0-7½	53	127	174	133	486	1091
	7½-30	99	147	238	121	605	
09-30-73	0-7½	48	148	109	84	389	983
	7½-30	32	25	244	293	594	
11-05-73	0-7½	55	354	396	230	1036	1621
	7½-30	39	196	189	161	586	
03-05-74	0-7½	110	293	188	82	673	
05-02-74	0-7½	93	555	514	429	1591	2003
	7½-30	2	134	158	119	412	
Inputs	06-09-73*	64	317	277	245		898
	11-05-73*	64	317	277	245		898
	TOTAL	128	634	553	491		1796

* Applied to deliver 1.12 kg/ha (tank delivery was not determined).

TABLE 4 WATERSHED 06 PARAQUAT* SUMMER 1974

Date	Depth cm	Grams paraquat remaining							
		Segments sampled beginning 05-22-74						Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Seg 5	Seg 6	Increment	0-30
(05-02-74 segments)		(3)	(4)		(1)	(2)			
	0-7 1/2	(514)	(429)		(93)	(555)		(1591)	(2003)
	7 1/2-30	(158)	(119)		(2)	(134)		(412)	
05-13, 14-74: Plowed (25 cm)									
05-22-74	0-7 1/2	134	122	124	156	140	83	759	4084
	7 1/2-30	771	322	679	771	453	329	3325	
05-30-74	0-7 1/2	179	124	155	175	102	176	912	2728
	7 1/2-30	425	391	174	326	170	330	1816	
07-03-74	0-7 1/2	231	144	195	258	153	131	1112	3973
	7 1/2-30	806	339	345	546	469	356	2861	
08-05-74	0-7 1/2	438	118	260	312	189	165	1482	
08-14-74	0-7 1/2	248	130	193	312	204	267	1354	4963
	7 1/2-30	607	509	531	759	691	512	3609	
09-03-75	0-7 1/2	267	211	148	296	239	126	1288	5108
	7 1/2-30	391	521	965	574	837	532	3820	
Inputs	05-22-74*	179	110	147	206	137	128		907
	To date	532	327	438	613	408	381		2702

* Based on tank delivery of 907 g (= 1.13 kg/ha).
Recovered on filter paper discs: 979 g (=1.22 kg/ha).

TABLE 5. WATERSHED 07 PARAQUAT* MAY 1973 TO MAY 1974

Date	Depth cm	Grams paraquat remaining				Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Increment	0-30
05-24-73	0-7½	0	0	0	0	0	0
06-09-73	0-7½	48	37	59	97	240	
06-18-73	0-7½	75	210	180	135	600	
07-04-73	0-7½	95	219	74	175	563	
08-11-73	0-7½	44	74	89	157	364	568
	7½-30	0†	17	34	152	204	
09-30-73	0-7½	58	86	38	229	410	1010
	7½-30	10	107	252	231	560	
11-05-73	0-7½	133	155	105	221	614	1068
	7½-30	66	106	110	173	454	
03-05-74	0-7½	144	299	275	---‡	717	
05-02-74	0-7½	183	244	187	431	1046	1469
	7½-30	47	0†	84	293	423	
Inputs	06-09-73*	82	164	122	245		613
	11-05-73*	82	164	122	245		613
	TOTAL	164	327	244	491		1225

* Applied to deliver 1.12 kg/ha (tank delivery was not determined).

† Minimum quantifiable was 50 ppb, equivalent to 12 g for 7½-30 cm in segment 1, and 24 g for segment 2.

‡ Not sampled.

TABLE 6. WATERSHED 07 PARAQUAT* SUMMER 1974

Date	Depth cm	Grams paraquat remaining — Segments sampled beginning 05-22-74 Seg 1	Seg 2	Seg 3	Seg 4	Seg 5	Seg 6	Sums Increment	0-30
(05-02-74 segments)		(3)	(4)		(1)	(2)			
	0-7 1/2	(184)	(244)		(187)	(431)	(1046)		(1469)
	7 1/2-30	(47)	(0)		(84)	(293)	(423)		-
05-13,14-74 Plowed (25 cm)									
05-22-74	0-7 1/2	109	53	77	68	61	101	469	2506
	7 1/2-30	698	268	281	366	164	261	2038	
05-30-74	0-7 1/2	149	64	103	134	66	114	628	1973
	7 1/2-30	291	143	205	168	199	339	1345	
07-03-74	0-7 1/2	192	100	125	176	104	156	852	2887
	7 1/2-30	296	204	298	564	302	371	2035	
08-05-74	0-7 1/2	221	93	174	197	97	200	982	
08-14-74	0-7 1/2	298	116	153	276	103	231	1176	3959
	7 1/2-30	425	475	295	777	321	490	2783	
09-03-74	0-7 1/2	207	127	150	163	153	142	963	3581
	7 1/2-30	553	251	363	601	314	556	2638	
Inputs	05-22-74*	176	71	110	120	71	130		678
	To date	554	222	347	378	222	409		2132

* Based on tank delivery of 678 g (= 1.24 kg/ha).
Recovered on filter paper discs: 481 g (= 0.88 kg/ha).

TABLE 7. WATERSHED 06 TRIFLURALIN* MAY 1973 TO MAY 1974

Date	Depth cm	Grams of Trifluralin remaining				Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Increment	0-30
05-24-73	0-7½	0	0	0	0	0	0
06-08-73	0-7½	8	34	71	30	143	
06-09-73	0-7½	83	179	501	355	1118	
06-18-73	0-7½	42	265	195	242	744	
07-04-73	0-7½	93	424	300	178	995	
08-11-73	0-7½	23	133	181	95	433	498
	7½-30	7	22	29	7	65	
09-30-73	0-7½	21	55	17	46	140	167
	7½-30	2	9	8	7	27	
03-05-74	0-7½	36	51	27	21	135	
05-02-74	0-7½	10	61	32	56	159	216
	7½-30	2	15	29	11	57	
Input	06-08-73*	64	317	277	245		898

* Applied to deliver 1.12 kg/ha (Tank delivery was not determined).

TABLE 8. WATERSHED 07 TRIFLURALIN* MAY 1973 TO MAY 1974

Date	Depth cm	Grams of Trifluralin remaining				Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Increment	0-30 cm
05-24-73	0-7½	0	0	0	0	0	0
06-08-73	0-7½	18	17	25	29	88	
06-09-73	0-7½	31	133	69	105	338	
06-18-73	0-7½	49	104	107	109	369	
07-04-73	0-7½	51	151	73	160	434	
08-11-73	0-7½	30	42	121	97	289	314
	7½-30	2	11	4	7	24	
09-30-73	0-7½	18	22	22	41	103	128
	7½-30	2	5	4	14	25	
03-05-74	0-7½	1	17	16	17	51	
05-02-74	0-7½	5	16	31	54	107	124
	7½-30	2	2	3	10	17	
Input	06-08-73*	82	164	122	245		613

* Applied to deliver 1.12 kg/ha (tank delivery was not determined).

catchments before 08-09-73. Nevertheless, during rains on 06-16 (2.49 cm) and on 06-25 to 06-29 (3.05 cm), runoff occurred from upper slopes and mid-row ponding occurred in central basin areas. Chemicals were undoubtedly displaced downslope and into the profile. Some loss of less persistent chemicals undoubtedly occurred by volatilization and degradation. These probable redistributions and losses are masked in segments 3 and 4 by a sampling bias which favored depositional intermediate slopes. Thus, the apparent constancy in total recoveries between 06-18 and 07-04 or 08-11-73 is an integrated expression of changes in distribution and variations in sampling recovery within segments and between segments in each watershed.

It is not possible to assess sampling recovery in soils of chemicals from later applications in this study because of uncertainties regarding background, especially after spring plowing. Sampling variation was certainly as great as that indicated by the filter paper discs. Random interception of chemicals from runoff on intermediate slopes and random patterns of cutting and sorted sedimentation along the central drainageway in each watershed would have contributed to sampling variation.

In spite of the indicated great variability in application and recovery, patterns of change over time appear which can be interpreted in terms of movement down slope or within the profile. Mass balance changes for individual chemicals are consistent with their known properties, and unique effects of topography and of soil and weather conditions are expressed.

Evidence for movement down slope and in the profile

Our sampling segments were laid out initially to differentiate between areas subject mainly to sheet erosion down the row and areas where cross-row rilling or visible sedimentation occurred. However, very fine sediments and dissolved chemicals can be intercepted, without visible evidence, by infiltration at any point down slope from areas of pickup. We had not anticipated the extent to which this could happen on the permeable sandy soils in these watersheds. Our composite samples in steeply sloping segments were based on 10 to 15 random cores but were, in effect, weighted in favor of depositional intermediate slopes.

Because of this sampling bias, increasing recovery in segments 3 and 4 of Fig. 6 and in segments 01, 03, 04 and 06 in Fig. 8 is evidence for downslope movement within these segments.

At upper elevations in the central drainageway, increasing recoveries will reflect interception from down-row runoff originating on slopes to the east and west. These areas would have been included in segments 2, 3 and 4 of Fig. 6 and in segment 02 of Fig. 8. Decreasing recoveries in these areas will reflect pickup in cross-row runoff, with displacement further downslope into segments 2 and 1 of Fig. 6 and into segment 05 of Fig. 8.

On areas of 4% slope or less at lower elevations along the central draw, increasing recoveries will reflect interception from both down-row and cross-row runoff. Major deposition would be expected in areas where mid-row ponding occurs frequently. Areas available for ponding are very different

in the two watersheds. Large differences can be expected between watersheds and between runoff events in interception and retention of chemicals in these areas. They are included in segment 1 and portions of segment 2 in Fig. 6 and in segment 05 of Fig. 8.

In all segments, losses by volatilization or degradation and by movement out of the sampling zone into the subsoil will contribute to decreasing recovery. Downward movement through the soil is more readily apparent in the original data for seven sampling depths, but it is reflected also in the data reported here for two depth categories (0-7-1/2 and 7-1/2 to 30 cm).

Paraquat in soils

It must be recognized that movement and retention in soils will reflect differences between chemicals in their partitioning between the solution phase and solid surfaces. A little known factor is the extent to which fulvic acid-type products of humification may influence the partitioning of even a strongly adsorbed chemical such as paraquat.

Paraquat was never detected in the water phase of runoff. However, concentrations less than 100 ppb in water were not detected routinely.

Thus, it cannot be assumed that paraquat moves only in association with particulate matter. Its retention and residual distribution in soils can, nonetheless, be interpreted in terms of interaction with adsorptive surfaces.

Our data for paraquat through summer 1974 are summarized in Tables 3 to 6. There is great variation from date to date for depths, segments and watershed sums. Included in this variation are variations associated with application, sampling and analysis, as well as random variation due to random patterns of pickup and interception which were not represented proportionately in 10 to 15 cores per segment.

Total recoveries on each watershed increased more rapidly than inputs. In the 09-03-74 sampling (Tables 4 and 6), recovery to 30 cm exceeded the total for three applications by 90% in watershed 06 and by 70% in 07.

Greater total recovery in 06 is related to the longer east-west slopes and the greater opportunity for interception of sediments and chemicals from down-row runoff. This relation to length of slope can be seen also within watersheds. Thus, during summer 1973, paraquat accumulated to higher levels in segment 3 of watershed 06 than in segment 4 (Table 3 and Fig. 6). In 07, the largest accumulation occurred in segment 4 (Table 5).

In the early growing season, interception on slopes is favored by the loose, uneven surface left by tillage operations. During winter and early spring, visible sedimentation is associated with lingering patches of snow or ice. On these watersheds, the last snow to leave was always on intermediate slopes where drifting occurred frequently and the insolation angle was low. Patterns of drifting varied with wind direction and were further influenced by a woodlot 50 meters directly south of the site and extending about 100 meters to the west of 07.

Marked accumulations of paraquat in surface layers (0-7-1/2 cm) of segments 2, 3 and 4 in the 05-02-74 sampling in watershed 06 (Table 3) were associated with a sequence of light snows (2 to 3 cm) in March. Between snows, the snow on upper and lower slopes would melt but a rather continuous snow or ice cover was maintained on intermediate slopes protected from the direct rays of the afternoon sun. Sediments were readily picked up by snowmelt and light rains on upper slopes because the surface soil remained saturated over frost. Frost was still present at 7 to 10 cm on 03-30-74. Visible sedimentation was observed where lingering snow and ice served to divert or slow down runoff part way down the slope.

In watershed 07, the greatest accumulation of paraquat on 05-02-74 was in surface layers of segment 4 where intermediate slopes were most protected from the direct rays of the sun during the warmer parts of the day. In segments 2 and 3, marked surface accumulations had occurred earlier in the winter, as indicated by our data for 03-05-74 (Table 5). By contrast, in watershed 06 (Table 3), paraquat in surface layers on 03-05-74 was sharply reduced from 11-05-73 in sloping segments and there was some evidence for net movement into segment 1. Such divergent wintertime sequences in the two watersheds reflect differences in patterns of drifting and disappearance of snow and frost as influenced by wind direction and mean incidence of insolation on major slopes.

In the absence of frost, paraquat moved quickly into the profile. Substantial movement to depths greater than 7-1/2 cm had occurred already by the time of our first full depth sampling on 08-11-73 (Tables 3 and 5). By 09-30-73, 60% of the total in both watersheds was in the 75% of sampled soil volume below 7-1/2 cm.

Due to the fall application on 11-05-73 and surface accumulation on frozen soil in depositional areas during the winter, the proportion below 7-1/2 cm was reduced to 20 or 30% in the 05-02-74 sampling. The surface accumulations were inverted by plowing so that, immediately after the spring application on 05-22-74, 80% of the total in both watersheds was found in the lower 75% of the sampling zone (Tables 4 and 6).

The first rains after the spring application occurred on 05-28-74 and 05-29-74 and totaled 1.96 cm. The soil was still moist from 1.17 cm of rain on 05-17 but loose and rough on the surface from discing and tillivator operations on 05-20. Most of the rain infiltrated where it fell, except for a brief period on 05-29 when ponding occurred in the 05 segments and a slight amount of runoff (140 l) was measured at the flume of watershed 07.

Our data for 05-30-74 suggest that 35 to 45% of the paraquat found below 7-1/2 cm on 05-22 may have been displaced by percolating water to depths below 30 cm. The greatest apparent losses into the subsoil occurred in segments with severely eroded slopes: 1, 3 and 4 in 06 (Table 4) and segment 1 in 07 (Table 06).

The indicated loss from deeper layers in segment 5 of watershed 06 was also great (60%). By contrast, there was no evidence for loss to the subsoil in segment 5 of watershed 07. This difference relates to the very much

larger areas in 06 where mid-row ponding can occur. Ponded water infiltrates into these sandy soils very quickly (unless frost is present). The soil in areas where ponding occurs is subject to more intense leaching of water-soluble pesticides than are soils on slopes where surface drainage is rapid.

After 05-22-74, watershed sums increased in each successive sampling through 08-14-74. The proportion found in the 75% of soil volume below 7-1/2 cm remained rather constant at 70 to 75% of the total for each watershed. Within individual segments, however, there were sequences of increasing and decreasing recovery in depth increments below 7-1/2 cm. These sequences occurred at different times in different segments but do not appear to be due simply to random variation. It appears that, within a given segment, there were periods of net movement into the plow layer from the surface and periods of net movement out of the lower plow layer into the subsoil.

The rapid movement of paraquat into the profile was not expected. Sifting of fine materials in the dry condition and infiltration and percolation of dissolved species and suspended matter would have been facilitated during early portions of each growing season by the loose condition of the plow layer, notably on eroded slopes. Cutting and filling in central areas would have contributed to in-depth distribution also. However, the principal factors affecting movement into and through the soil would appear to be topographical features, variations in soil structure, and the presence or absence of frost or of a vigorously growing crop, which determine net infiltration and deep percolation of water.

The evidence that extensive movement occurred in association with ponding through the essentially structureless fine sands of segment 5 in watershed 06 suggests that paraquat may have moved to a large extent in solution, perhaps in association with solubilizing organics in the fulvic acid fraction of soil organic matter. Paraquat adsorbed on suspended clay or silt fractions would move readily into the granular plow layer on eroded slopes but would tend to be intercepted at the plow sole, which is included in our deepest sampling increment (22-1/2 to 30 cm). Our data provide no clear evidence of progressive build-up at this depth.

Due to our sampling bias which favored depositional slopes, increasing recoveries of paraquat in our steeply sloping segments actually reflect down-slope displacement. With this in mind, the data in Tables 4 and 6 present a picture of progressive down-slope displacement of paraquat in runoff, with interception and infiltration into the soil on intermediate slopes in segments 1, 2, 3, 4 and 6 and in areas of ponding in segment 5. Differences between the two watersheds reflect mainly differences in length of E-W slope and the proportion of gentle slopes where runoff flows tend to slow down or where mid-row ponding can occur.

It is apparent that the sandy soils on these watesheds have a limited capacity for retaining paraquat. Although our total recoveries through 09-03-74 still exceeded inputs, it appears that substantial movement into the subsoil had occurred. Losses into the subsoil undoubtedly exceed, by a large factor, losses in runoff at the catchments. The concentration of dissolved and suspended paraquat in percolating water is probably not greatly

different from that in normal runoff. During the more intense runoff events, the heavier sediments picked up will tend to be less adsorptive and contribute proportionately less to runoff losses of paraquat.

By the end of summer 1974, both watersheds appeared to be approaching a steady state where, with twice-a-year inputs of paraquat, the total retained in the plow layer over each watershed will reflect mainly seasonal or annual differences in rainfall and net percolation. Within individual segments, large fluctuations in total recovery and depth distribution will reflect effects of topographical features, frost, tillage operations and crop on interception, infiltration and deep percolation of precipitation and runoff. Variation associated with these factors appears to be well in excess of random variation, although anomalous data points do appear and will need to be given special statistical treatment.

Trifluralin in soils

Because of the volatility of trifluralin, the first mass balance sampling was taken on 06-08-73, immediately after the trifluralin was applied and worked in to 3 inches with a tillivator (Tables 7 and 8). These samples were taken as single depth increments to 7-1/2 cm. On the following day, after application of paraquat and diphenamid, soils were sampled again in four increments to the same depth.

Trifluralin was encountered at all four depths on 06-09. The sum for the four increments was 3 to 4 fold greater than in the single increment taken the previous day. The lower recoveries in the single in-rement of 06-08 may reflect losses of very dry fine materials during sample manipulation, since a strong wind came up shortly after application. It was windy also on 06-09, increasing the likelihood for contamination as deeper increments were exposed, in sampling, to fine materials blowing across the soil surface.

The largest recoveries of trifluralin at lower depths on 06-09-73 were in segment 2 of both watersheds and in eroded segment 3 of 06 and 4 of 07. In the same samples, varying proportions of paraquat and diphenamid were also encountered at depths below the surface centimeter. Since these two chemicals were not worked in, recovery at deeper levels must be attributed to contamination. There was a tendency to deeper recovery of all three chemicals in eroded segments where the plow layer is coarsely granular due to incorporation of subsoil materials. As samples were being taken, fine, dry materials sifted readily downward into this loose, open structure but were intercepted whenever moist soil was encountered. In all segments, variation in recovery with depth in this sampling likely reflects variation in rate of drying and distribution of moisture in the freshly tilled upper plow layer.

Due, at least in part, to its high volatility, trifluralin is the least persistent in soils of the chemicals in this study. Kearney et al. (1969) give 6 months for 75 to 100% disappearance. A discussion of factors affecting trifluralin volatization is given by Harper et al. (1976).

There is no evidence of net loss from either watershed through 07-04-73 (Tables 7 and 8). Losses due to volatilization and degradation undoubtedly

occurred but were masked by downslope movement and our sampling bias in steeply sloping segments. Net accumulation had occurred by 07-04 in segment 2 of watershed 06 and segments 1 and 4 of 07.

Total recoveries declined sharply during July through September and then remained rather constant through the winter (no fall application was made). As in the case of paraquat, deposition associated with snow and ice on intermediate slopes served to maintain or increase recoveries in segments 3 and 4 of both watersheds and, to a lesser extent, in segment 2. Net losses occurred between 09-30-73 and 05-02-74 in the segments nearest the catchments (segment 1, Fig. 6).

The original data show major losses over the year from surface increments (0 - 1, 1 - 2-1/2, 2-1/2 - 5 cm). There is some evidence for progressive downward displacement of residual trifluralin at lower depths. Movement within the plow layer after 06-09-73 was, however, very slow as compared with paraquat. Net movement into the subsoil would appear to have been negligible. This relative immobility of residual trifluralin is consistent with its very low solubility (<1 ppm at 27° C).

Diphenamid in soils

The solubility of diphenamid (260 ppm at 26° C) (Herbicide Handbook, 1974) is much less than for paraquat but substantially greater than for trifluralin. It is essentially non-volatile and, perhaps for this reason, it is considered to be somewhat more persistent in soils than trifluralin (8 months vs 6 months for 75 to 100% disappearance).

Only about 1/3 of the first application of diphenamid was recovered in the 06-09-73 sampling (Tables 9 and 10). In the original data, most of the recovery was in the upper three increments (0 - 1, 1 - 2-1/2, 2-1/2 - 5 cm). As in the case of paraquat and trifluralin, a large proportion was recovered below the surface centimeter or two in eroded segments 3 of 06 and 4 of 07.

After 06-09-73, total recoveries remained rather constant through 08-11 on 06 and through 07-04 on 07. Increasing recoveries in segments 1, 2 and 3 of 06 through 08-11 are evidence for extensive down-slope displacement. The evidence for watershed 07 is less clear, but deposition on intermediate slopes would have served to counter degradation losses and maintain recoveries in segments 2, 3 and 4.

Diphenamid moved into the plow layer more rapidly than trifluralin. By 09-30-73, there was evidence of movement to depths below 7-1/2 cm in segment 3 of 06 (Table 9). During the winter, recoveries below 7-1/2 cm increased markedly in all segments of 06. The original data indicate some diphenamid may have been lost from the plow layer into the subsoil.

The indicated downward movement of diphenamid during the winter contrasts with the behavior of paraquat, which appeared to have moved very little within the plow layer, while marked surface deposition occurred in association with lingering snow and ice on intermediate slopes (cf. Table 3). Diphenamid is much less strongly adsorbed than paraquat and could have moved

TABLE 9. WATERSHED 06 DIPHENAMID* MAY 1973 to MAY 1974

Date	Depth cm	Grams of Diphenamid remaining				Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Increment	0-30
05-24-73	0-7½	0	0	0	0	0	
06-09-73	0-7½	95	270	475	73	913	
06-18-73	0-7½	46	182	190	290	707	
07-04-73	0-7½	47	316	411	164	938	
08-11-73	0-7½	92	351	326	141	911	938
	7½-30	2	9	8	7	27	
09-30-73	0-7½	11	31	122	77	240	424
	7½-30	2	9	165	7	184	
11-05-73	0-7½	38	211	66	175	490	517
	7½-30	2	9	8	7	27	
03-05-74	0-7½	24	58	95	95	272	
05-02-74	0-7½	11	38	25	11	85	491
	7½-30	35	173	125	74	406	
Inputs	06-09-73*	192	951	830	736		2695
	11-05-73*	192	951	830	736		2695
	TOTAL	383	1902	1660	1472		5389

* Applied to deliver 3.36 kg/ha (tank delivery was not determined).

TABLE 10. WATERSHED 07 DIPENNAMID* MAY 1973 TO MAY 1974

Date	Depth cm	Grams of Diphenamid remaining				Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Increment	0-30
05-24-73	0-7 1/2	0.0	0.0	0.0	0.0	0.0	
06-09-73	0-7 1/2	36.0	183.6	62.2	164.0	445.8	
06-18-73	0-7 1/2	63.8	125.3	175.8	222.2	587.2	
07-04-73	0-7 1/2	27.6	154.3	84.4	178.0	444.3	
08-11-73	0-7 1/2	27.1	105.0	28.3	108.0	268.4	300.6
	7 1/2-30	2.4	4.8	8.3	16.7	32.2	
09-30-73	0-7 1/2	15.8	41.8	15.0	76.2	148.8	166.9
	7 1/2-30	2.4	4.8	3.6	7.3	18.1	
11-05-73	0-7 1/2	188.3	516.3	352.4	543.1	1600.1	1653.6
	7 1/2-30	2.5	4.8	39.0	7.2	53.5	
03-05-74	0-7 1/2	9.3	18.7	11.2	104.6	143.9	
05-02-74	0-7 1/2	9.8	16.5	5.1	7.9	39.3	141.8
	7 1/2-30	10.6	38.7	30.6	22.6	102.5	
Inputs	06-09-73*	245	491	366	736		1838
	11-05-73*	245	491	366	736		1838
	Total	491	981	732	1472		3676

* Applied to deliver 3.36 kg/ha (tank delivery was not determined).

rapidly with percolating water during winter thaws, when the frost layer recedes or disappears altogether, as snow cover is removed exposing bare soil to the direct rays of the sun.

During this first year, movement of residual diphenamid within the plow layer was less in watershed 07 than in 06. The evidence in the original data and in Table 10 indicates that movement into the subsoil was also less in 07.

After the 11-05-73 application, diphenamid inputs were discontinued on watershed 06, and no analyses were made after 05-02-74. Data following the 05-22-74 application on 07 are presented in Table 11.

Diphenamid disappeared much more rapidly in 1974 than the previous summer. It is likely that degradation losses were greater due to adaptations in soil microbial populations. However, leaching and runoff were also greater. The original data indicate that substantial quantities of diphenamid moved through the plow layer into the subsoil. As in the case of paraquat, major movement out of the granular plow layer in segment 1 occurred between 05-22 and 05-30 (cf. Tables 6 and 11).

In other segments, diphenamid residues were retained within the sampling zone for longer periods than in segment 1 (Table 11). Longer retention in sloping segments 3, 4 and 6 reflects differences in infiltration capability during early rains and differences in grade and length of E-W slopes, allowing for interception and infiltration of runoff on intermediate slopes over a succession of events (Figs. 2 and 8). Repeated inputs from runoff from higher slopes served to maintain detectable quantities of diphenamid within the sampling zone in segments 4 and 5 through the final sampling on 09-03.

Atrazine in soils

Atrazine is somewhat less soluble than diphenamid (30 to 70 ppm vs 260 ppm) (Herbicide Handbook, 1974). It is generally considered to be somewhat more persistent in soils also (10 months vs 8 months for 75 to 100% disappearance).

Ten annual applications had been made for corn on these watersheds before this study was initiated in spring 1973. Carryover from these earlier applications would explain the presence of atrazine in all depth increments to 30 cm immediately after the 05-22-74 application on watershed 06 (Table 12). Sixty percent of the total was found in the 0 - 1 cm increment, and this represents 64% recovery of the calculated tank delivery. The soils were moist to the surface at the time of application. We did not have the sampling difficulties encountered in very dry soils at the time of the initial samplings in 1973. We are confident that very little contamination of increments below the surface centimeter occurred.

It is unfortunate that analyses for background atrazine were not made prior to the 05-22-74 application. It is difficult to reconcile the apparent persistence of atrazine (from the last previous application in 1972) with

TABLE 11. WATERSHED 07 DIPHENAMID* SUMMER 1974

Date	Depth cm	Grams diphenamid remaining Segments sampled beginning 05-22-74 Seg 1	Seg 2	Seg 3	Seg 4	Seg 5	Seg 6	Sums Incre-ment	0-30
(05-02-74 segments)		(3)	(4)		(1)	(2)			
	0-7 1/2	(5)	(8)		(10)	(16)	(39)		(142)
	7 1/2-30	(31)	(23)		(11)	(39)	(102)		
05-13,14-74	Plowed (25 cm)								
05-22-74	0-7 1/2	392	167	166	169	66	213	1174	1991
	7 1/2-10	463	26	125	97	12	94	817	
05-30-74	0-7 1/2	370	83	173	155	60	210	1052	1399
	7 1/2-30	178	40	88	156	10	75	547	
07-03-74	0-7 1/2	32	6	24	35	18	42	157	368
	7 1/2-30	52	18	13	34	8	86	211	
08-05-74	0-7 1/2	9	0	30	63	26	33	160	
08-14-74	0-7 1/2	0†	0	0	1	14	34	49	463
	7 1/2-30	18	0	0	175	92	129	414	
09-03-74	0-7 1/2	0	0	0	0	11	0	11	73
	7 1/2-30	0	0	0	54	8	0	62	
Inputs	05-22-74*	530	213	332	362	213	392		2040
	To date	1484	596	930	1014	596	1097		5716

* Based on tank delivery of 2040 g (= 3.73 kg/ha).
Recovered on filter paper discs: 1619 g (= 2.96 kg/ha).

† Minimum detectable (15 ppb) for 0-7½ / 7½-30 cm: Seg 1 (2 g / 7 g), Seg 2 (1 / 3), Seg 3 (1 / 4), Seg 4 (1 / 5), Seg 5 (1 / 3), Seg 6 (1 / 5).

TABLE 12. WATERSHED 06 ATRAZINE* SUMMER 1974

Date	Depth cm	Grams Atrazine remaining						Sums	
		Seg 1	Seg 2	Seg 3	Seg 4	Seg 5	Seg 6	Incre-ment	0-30
		Segments sampled beginning 05-22-74							
05-22-74	0-7 1/2	586	399	370	634	506	235	2731	3768
	7 1/2-30	130	114	232	302	134	125	1037	
05-30-74	0-7 1/2	353	324	270	433	256	262	1898	1961
	7 1/2-30	9	3	11	16	12	12	63	
07-03-74	0-7 1/2	185	57	76	140	84	75	618	634
	7 1/2-30	0†	4	8	0	0	4	16	
08-05-74	0-7 1/2	106	69	69	226	97	84	651	
08-14-74	0-7 1/2	20	24	47	70	50	81	292	299
	7 1/2-30	0	0	7	0	0	0	7	
09-03-74	0-7 1/2	64	52	39	61	58	48	322	424
	7 1/2-30	7	24	0	0	71	0	102	
Input	05-22-74*	714	438	588	823	547	511		3625

* Based on tank delivery of 3625 g (= 4.52 kg/ha).
Recovered on filter papers discs: 3160 g (= 3.94 kg/ha).

† Minimum detectable (5 ppb) for 0-7½ / 7½-30 cm:
Seg 1 (0.7 g / 2.6 g), Seg 2 (0.4 / 1.6), Seg 3 (0.5 / 2.1), Seg 4 (0.8 / 3.0),
Seg 5 (0.5 / 2.0), Seg 6 (0.5 / 1.9).

its rapid disappearance from the lower plow layer between 05-22 and 07-03-74. Nevertheless, the freshly tilled soil was favorable for infiltration of rainfall. Moreover, there was evidence that substantial quantities of paraquat in both watersheds and of diphenamid in 07 were displaced into the subsoil during this period also.

Carryover atrazine from earlier applications had virtually disappeared from the lower plow layer by 07-03-74. Residual atrazine from the 05-22-74 application moved progressively downward through the four increments above 7-1/2 cm and was found in the 7-1/2 - 15 cm increment of segments 1, 2 and 5 in the last sampling of 09-03-74. Direct comparison cannot be made between atrazine and diphenamid since they were not applied together on the same watershed. However, comparison of data in Tables 11 and 12 suggest that atrazine was less mobile in soils than diphenamid, as might be expected from its lower solubility. (The evidence on this point is more obvious in the original data where movement through the 7 sampling levels can be followed).

As in the case of diphenamid, degradation losses served to obscure evidence for movement downslope. Soil populations adapted to degrading atrazine would have been present after ten annual applications. Interception and accumulation on intermediate slopes and in central basin areas failed to keep pace with disappearance. Larger quantities of atrazine than of diphenamid were retained in the 09-03 sampling, which is consistent with reported differences in their persistence (cf. Tables 11 and 12).

Summation

This preliminary assessment of our soil core data through summer 1974 has revealed a number of relationships to methodology, chemical species, topography, soil conditions and weather which should be helpful in interpreting and modeling these and later data through summer 1975.

a) Random variation is high and derives from variable distribution of chemicals during application, variability associated with sampling and analysis, and random patterns of pickup and interception from runoff.

b) Useful variation is present and can be interpreted in terms of movement downslope and within the plow layer and in terms of loss by degradation and/or volatilisation or by leaching out of the sampling zone into the subsoil.

c) Due to sampling bias, downslope movement within steeply sloping segments is reflected by increasing recovery rather than by decreasing mass balances as might be expected. This relationship may change if the capacitances represented by depositional slopes and by retention in the plow layer are satisfied or exceeded by heavier rainfall in 1975.

d) Because of its resistance to degradation and its susceptibility to adsorption, paraquat was the most useful tracer

for following movement and retention in the landscape. Losses by degradation or volatilization tended to mask the evidence for movement of other herbicides in this study.

e) Mobility was related directly to solubility: paraquat > diphenamid > atrazine > trifluralin. The great mobility of paraquat was not expected and suggests interactions with mineral and organic colloids and soluble fulvic acid components which inhibit its biological activity without immobilizing it.

f) Redistribution patterns reflected the effects of a number of factors on interception, infiltration and deep percolation of rainfall and runoff. East-west planter rows determined the direction of runoff from upper slopes, promoted cascading cross-row runoff in the central drainageway, and provided micro-relief for impoundment of runoff (with sorted sedimentation) at lower elevations. Granular structure of the plow layer on eroded slopes promoted infiltration and deep percolation of rainfall and runoff. Loosened structure and irregular surface of freshly tilled soil promoted interception and infiltration during earlier portions of each growing season. Length and pitch of slope were important, as well as exposure of slope to drifting snow and winter sun. The presence of a frost layer precluded deep percolation, promoted pickup of saturated soil materials on upper slopes and ponding at lower elevations. Lingering snow and ice promoted interception on intermediate slopes.

g) Differences between the two watersheds in distribution and retention of chemicals reflected mainly differences in length of E-W slopes and the proportion of gentle slopes where runoff flows tend to slow down or where ponding can occur. Soil differences were minor except in relation to topography and the degree of erosion and incorporation of granular subsoil materials into the plow layer.

h) Movement over the watersheds and through the soil was more rapid in summer 1974 than in 1973, reflecting rains of greater magnitude. In 1975, deeply penetrating rains and rains of erosive intensity were more frequent than in 1974. Greater downslope movement of chemicals may be expected because visible sediments were transported further down the drainageway in both watersheds. Corn and soybeans were much more vigorous in 1975, and differences between watersheds may reflect differences in nature of the canopy and its rate of development.

Selected Runoff Data, 1975

Our objective in this section is to illustrate how weather sequences which precede a runoff event influence the capacity of soils to accept rainfall or to intercept runoff which contains potential pollutants.

During the growing season, even light rains can serve to slake surface aggregates and level off irregularities left by tillage, thereby reducing infiltration capacity and facilitating runoff during later events. Penetrating rains, by satisfying the waterholding capacity of the soil, will increase the likelihood of runoff when it rains again. This will be true in particular during the period when surplus gravitational water is retained in the soil. On the permeable soils in these watersheds, the difference between runoff and no runoff during Spring, Summer, and Fall was frequently determined by rain which occurred 24 to 36 hours before the rain which actually produced runoff. During the wintertime, runoff volumes and sediment loads were influenced by weather sequences, extending over periods of days or weeks, which determined the depth and distribution of snow, ice, and frost.

An effort was made during winter 1974-75 to record snow, ice, and frost conditions in greater detail than during the previous winter. These observations and associated weather conditions are summarized for important sequences of events in Tables 13 to 16. Precipitation summaries for these events and runoff data for watershed 06 are presented in Tables 19 to 22.

Two major historic rainfall events were experienced in 1975, one on bare soil in April and one in August when vigorous, fully developed crop cover was present. Significant soil conditions and weather sequences associated with these events are summarized in Tables 17 and 18. Precipitation summaries and runoff data for both watersheds are summarized in Tables 23 and 24.

Runoff and residue data in Tables 19 to 24 have been calculated by interpolating linearly between points on the waterstage calibration curve. Runoff volumes integrated by the computer will be more accurate, but our calculations are adequate for our objective in this section.

Wintertime runoff sequences

Beginning late in NOvember 1974, the surface soil would freeze overnight or for periods of days but would thaw during periods of rain or melting snow. Thus, the soil remained permeable, and no runoff occurred until 01-08 to 01-10-75 when a combination of snow melt and rain totalling 2.74 cm did produce runoff at the catchments. On 01-10-75, there was no evidence of frost to 30 cm.

Immediately following these first wintertime events, there was a two-week period of very cold weather (night temperatures ranging down to -20 C). Snow cover was light (0 to 2-1/2 cm), and the soil froze deeply. Major runoff events from late January through February occurred on frozen soil and were due to rain or melting snow or a combination of snow melt plus rain. During this period bare soil areas or areas under thin and aging (granular)

TABLE 13. WEATHER AND WATERSHED CONDITIONS FOR THE PERIOD 03-12-75 TO 03-11-75

Daily runoff due to snow melt on soil initially frozen to 46 cm (18 in).

02-13-75	Five to ten centimeters snow on soil frozen from surface to 46 cm. Air temperature rose from -4° C (25° F) overnight to 3° C (38° F) at about 1600. Rained in a.m. (.18 cm) from 0530 to 0630, but runoff due to snow melt did not start until 1300.
03-13-75	Air temperature rose from overnight low of -8° C (18° F) to maximum of 2° C (35° F) at about 1600. Runoff due to snow melt began at 1000 continued to 1930. Runoff flowed under crusted snow and ice, over frozen soil beginning to thaw (1.25 cm) by late p.m.
03-14-75	Air temperature rose from overnight low of -7° C (20° F) to maximum of 0° C at about 1600. Runoff due to snow melt (bright sun) began at 1225 and continued to 1810. Runoff flowed under crusted snow and ice (2.5 cm) over frozen soil beginning to thaw (1.25 cm) again in p.m.
03-15-75	Air temperature rose from overnight low of -8° C (18° F) to a maximum of 6° C (43° F) in p.m. Runoff due to snow melt began at 1100 and continued to 1850. Areas of bare soil appearing and thawing rapidly, but saturated to surface.
03-16-75	Air temperature rose from overnight low of -3° C (27° F) to maximum of 7° C (45° F) at about 1400. Runoff due to snow melt began at 0930 and continued to 2000. Only patches of snow left. Soil thawed to depth of 5 to 7 cm.
03-17-75	Air temperature rose from overnight low of -3° C (27° F) to maximum of 11° C (52° F) in p.m. Runoff due to melting of patches of snow remaining on intermediate slopes began at 0916. All snow had disappeared by 1100, but runoff due to seepage from saturated surface soil continued to 1345. Surface soil was thawed to depth of 7 cm, but frozen below that to depths greater than 30 cm.

TABLE 14. WEATHER AND WATERSHED CONDITIONS FOR THE PERIOD 03-18-75 TO 03-24-75

Thawing sequence followed by snow and rain producing runoff over thawed plow layer over frozen subsoil.

03-18 to 03-21-75	Daily maximum air temperatures ranged from 10 to 13° C (50 to 55° F) and daily minimums from -2° C to 4° C (28 to 39° F). Soil was bare and thawing at rate of 2 to 5 cm. per day. Plow layer (0-25 cm.) had thawed by 03-22-75, but subsoil was still frozen to 46 cm. There was .08 cm rain on 03-19 and 1.47 cm rain equivalent as snow changing to rain in A.M. of 03-21. Snow depth of 10 cm. was observed in A.M., 5 to 7 cm at 1400 and 2.5 cm at 1700 on 03-21. Thawed plowed layer took up rain and snow melt without runoff.
03-22-75	Air temperature rose from overnight low of 0° C to maximum of 7° C (44° F) in P.M. Snow from 03-21 disappeared during the night. Runoff from snow melt began at 0144. Seepage from saturated plow layer probably contributed also. Runoff increased sharply following each of three showers between 0445 and 0750. Scattered light showers continued to 0950, for a total of 1.12 cm. Runoff continued to 1058.
03-23 to 03-24-75	Air temperature rose from overnight low of -2° C (29° F) to maximum of 9° C (48° F) in P.M. of 03-23, dropped to 1° C (33° F) during the night, then rose to a maximum of 16° C (61° F) on 03-24. Scattered showers from 2055 on 03-23 to 0550 on 03-24 (total 0.81 cm) produced runoff beginning 2156 and continuing to 0830. Plow layer was near saturation from the precipitation of 03-22 and there was still frost in the subsoil.

TABLE 15. WEATHER AND WATERSHED CONDITIONS FOR THE PERIOD 03-25-75 TO 03-31-75

Freezing sequence followed by rain and snow producing runoff over frozen soil subject to diurnal thawing and freezing at the surface.

03-25 to 03-27-75	Low night temperatures (-3 to -8° C or 18 to 27° F) created new frost layer which would thaw during the day to a depth of 2.5 cm (daily maximum air temperature on 03-26 and 03-27 was 0° C). There were traces of snow each day.
03-28 to 03-29-75	Air temperature rose from overnight low of -3° C (26° F) to maximum of 2° C (36° F) in early P.M. of 03-28. Light drizzle beginning at 1540 and continuing intermittently to 0320 on 03-29 (total 0.53 cm) produced runoff beginning at 1904 on 03-28 and continuing to 1408 on 03-29. Runoff occurred over soil thawing and saturated at the surface. Frost was encountered at depth of 2.5 cm at end of event (1400 on 03-29).
03-30-75	Air temperature dropped to -7° C (20° F) during night of 03-29, producing about 2 cm of snow (equivalent to 0.20 cm rain). Snowfall began about midnight and continued to 1330. Temperature rose by noon on 03-30 to 0° C maximum for the day. Runoff due to snow melt began at 1252 and continued to 1544. Runoff was terminated by falling temperature.
03-31-75	Air temperature rose from overnight low of -9° C (15° F) to maximum of 9° C (49° F) at about 1400. Runoff due to snow melt began at 1334 and continued to 1750. Runoff was terminated by falling temperature and by the fact that essentially all of the snow had melted.

TABLE 16. WEATHER AND WATERSHED CONDITIONS FOR THE PERIOD 04-01-75 TO 04-13-75

	Heavy snow (33 cm), followed by high winds and drifting, 5 days of freezing and 6 days of daily runoff due to snow melt on soil initially frozen to 15 cm.
04-01 to 04-07-75	Watershed was bare on 04-01. Snowfall beginning in early A.M. of 04-02 and continuing through 0545 on 04-03, equivalent to 2.26 cm rain, deposited 33 cm of snow. Severe drifting on 04-04 left variable snow cover (5 to 20 cm) on watershed and buried collection facilities (drifts of 2 to 2 ½ m.). Low night temperatures -7 to -10° C (13 to 19° F) from 04-03 to 04-07 froze soil to 15 cm. Below 15 cm, earlier frost had disappeared (unfrozen to 60 cm), except frozen soil was encountered at 30 cm in one core on a steep northerly slope which receives winter sun at a very narrow angle of incidence. Bright sun and maximum air temperatures of 1° C on 04-05, 2° C on 04-06 and 5° C on 04-07 melted snow on upper slopes, producing runoff which was intercepted by snow on lower slopes but beginning to pond in confluence area (segment 5) on 04-07. Under snow cover, soil remained frozen to surface but began to thaw quickly wherever the snow cover was reduced to a thin crust.
04-08 to 04-13-75	This was a period of daily runoff due to melting of snow from 04-02 and 04-03. No precipitation, bright sunny days with daily maxima of 3° to 9° C (37° to 48° F), overnight lows of -3° to -5° C (22° to 27° F). Soil on lower slopes and over much of confluence area remained frozen to surface under snow or in bare soil areas where saturated soil was subject to nightly freezing. On bare upper slopes, frost had disappeared through the plow layer by 04-11. Daily runoff declined on 04-12 and 04-13 as snow and frost disappeared from confluence areas, permitting soil to drain and accept continuing snow melt from drifts on lower slopes.

TABLE 17. WEATHER AND WATERSHED CONDITIONS FOR THE PERIOD 04-14-75 TO 04-18-75

Sunny days and rising temperatures, culminating in historic rainfall event on bare soil (corn stubble on Watershed 06, soybean stubble on 07).

04-14 to 04-17-75 This was a period of sunny days and rising temperatures (daily maxima rose from 8° C (47° F) on 04-14 to 16° C (60° F) on 04-17, overnight lows did not go below freezing and went only to 10° C (50° F) during night of 04-17. A few small patches of crusted snow and ice remained on north-facing steep slopes in A.M. of 04-18. Elsewhere, frost had disappeared, soils had drained and were dry or drying at the surface.

04-18-75 Air temperature rose from overnight low of 10° C (50° F) to maximum of 19° C (66° F) at 1700. The temperature maximum was preceded by light rains beginning at 1320. At 1700, heavy rain (5-min. intensities up to 7.4 cm per hour) began and continued without interruption to 2200, after which light rains continued to 2400. Total for the event (10.95 cm = 4.31 inches in 10 hours) represents a long term historical extreme. It produced major flooding in the Lansing area--the worst since 1947. Severe washing and gullying occurred on the watersheds. An estimated 1400 kg of coarse sediment was deposited in the catchment. Similar quantities of intermediate particle size sediment were deposited in the after flume drainage channel; these represented back-up water tapped off at intervals by hand directly through the sample splitter which was under water. Actual loss of sediment from the watershed was likely 3-fold (or more) greater than can be calculated from our runoff data.

TABLE 18. WEATHER AND WATERSHED CONDITIONS ON 08-21-75 AND 08-22-75

Historic rainfall event on soil under fully developed corn (Watershed 06) or soybeans (Watershed 07).

08-21-75 This was a major historical growing season event. The USWB report shows 2.46 inches (6.25 cm) for the 24-hours ending at 1700 on 08-21. Of this total, 0.51 cm came as a light drizzle beginning at 1720 on 08-20 and continuing to 0320 on 08-21. This rain served to saturate the canopy and slake surface soil prior to near-record rainfall beginning at 1300 and continuing to 1910 (5.95 cm = 2.35 inches in 6 hours, with 5-min intensities up to 16.15 cm/hour). In spite of the cover provided by vigorous, fully developed crops of corn and soybeans (better than average for these watersheds), extensive washing and gulleying occurred and sediment losses were substantial.

08-22-75 This event occurred while soils were still well charged with water from the very heavy rain of 08-21. Runoff data for the two watersheds serve to illustrate unique features, related to canopy and topography, which influenced runoff and losses of sediments and chemicals.

TABLE 19. RAINFALL, RUNOFF AND PESTICIDES IN RUNOFF FOR THE PERIOD 03-12-75 TO 03-17-75

Date	Rain				Watershed 06										
					Runoff		Sediment		Paraquat				Atrazine		
	Duration	2-min max	5-min max	10-min max	Duration	Max flow	No. of samples	Mean	Sed	H_2O	Kd*		Sed	H_2O	Kd
	hr	cm/hr	cm/hr	cm/hr	hr	L/min		g/L	ppm	ppm			ppm	ppm	
03-12-75	--- (Snow melt)---				15.7	49	2	0.2	14.8	<0.1	148+		.53	.007	76
03-13-75	--- (Snow melt)---				9.5	69	4	0.4	26.2	<0.1	262+		2.43	.027	91
03-14-75	--- (Snow melt)---				5.7	12	1	0.5	29.5	<0.1	295+		1.40	.034	41
03-15-75	--- (Snow melt)---				8.2	192	4	2.9	14.4	<0.1	146+		1.72	.045	38
03-16-75	--- (Snow melt)---				10.5	40	(No samples. Equipment breakdown.)								
03-17-75	--- (Snow melt)---				4.5	24	1	1.7	20.4	<0.1	206+		1.50	.115	13

	Total rain	Total runoff	Total sed.	Total paraquat			Total atrazine		
				Sed	H_2O	Sum	Sed	H_2O	Sum
	cm	Liters	Kg.	g			g		
03-12-75	0.0	13,881	2.4	.04	1.37	1.41	<.01	.10	.10
03-13-75	0.0	12,938	5.7	.15	1.28	1.43	.01	.34	.36
03-14-75	0.0	1,986	1.1	.03	.20	.23	<.01	.07	.07
03-15-75	0.0	29,992	87.4	1.26	2.97	4.23	.15	1.36	1.51
03-16-75	0.0	5,668	(No Samples.)	---	---	---	---	---	---
03-17-75	0.0	1,772	3.1	.06	.18	.24	.01	.20	.21

*Kd = $\frac{\text{ppm in sediment}}{\text{ppm in } H_2O}$

TABLE 20. RAINFALL, RUNOFF AND PESTICIDES IN RUNOFF FOR THE PERIOD 03-18-75 TO 03-24-75

Date	Rain				Watershed 06									
					Runoff		Sediment		Paraquat			Atrazine		
	Duration	2-min max	5-min max	10-min max	Duration	Max flow	No. of samples	Mean	Sed	H_2O	Kd*	Sed	H_2O	Kd
	hr	cm/hr	cm/hr	cm/hr	hr	L/min		g/L	ppm	ppm		ppm	ppm	
03-19-75	1.0	.76	.30	.15	(Rain, No runoff)									
03-21-75	6.2	1.52	.91	.76	(4" snow, changing to rain. No runoff)									
03-22-75	5.1	1.52	1.22	.91	9.2	1,273	8	2.8	19.6	<0.1	198+	1.21	.029	42
03-23-75 to 03-24-75	7.9	1.52	1.22	.76	10.6	653	7	5.3	24.3	<0.1	245+	.86	.028	31

	Total rain	Total runoff	Total Sed	Total paraquat			Total atrazine		
				Sed	H_2O	Sum	Sed	H_2O	Sum
	cm	Liters	Kg	g			g		
03-19-75	0.08	———	——	—	—	——	—	—	—
03-21-75	1.47	———	——	—	—	——	—	—	—
03-22-75	1.12	85,225	242.2	4.74	8.44	13.18	.29	2.45	2.74
03-23-75 to 03-24-75	0.81	35,333	188.8	4.59	3.50	8.09	.16	.99	1.15

*Kd = $\frac{\text{ppm in sediment}}{\text{ppm in } H_2O}$

TABLE 21. RAINFALL, RUNOFF AND PESTICIDES IN RUNOFF FOR THE PERIOD 03-25-75 TO 03-31-75.

Date	Rain				Watershed 06										
					Runoff		Sediment		Paraquat			Atrazine			
	Duration	2-min max	5-min max	10-min max	Duration	Max flow	No. of samples	Mean	Sed	H_2O	Kd*	Sed	H_2O	Kd
	Hr	cm/hr	cm/hr	cm/hr	hr	L/min		g/L	ppm	ppm		ppm	ppm	
03-25-75 to															
03-27-75	(Traces of snow, low night temperatures, new frost layer deepening daily.)														
03-28-75 to															
03-29-75	14.8	.76	.30	.33	19.1	350	3	1.4	15.4	<0.1	156+	.52	.017	31	
03-30-75	0.2	.76	.30	.15	(Three-fourths inch of snow during A.M.)										
	—— (Snow melt)————				2.9	40	2	1.9	22.7	<0.1	229+	.83	.037	28	
03-31-75	—— (Snow melt)————				4.3	117	(No Samples. Equipment iced up.)								

	Total rain	Total runoff	Total sed	Total paraquat			Total atrazine		
				Sed	H_2O	Sum	Sed	H_2O	Sum
	cm	Liters	Kg	g			g		
03-28-75 to									
03-29-75	0.53	22,586	32.6	.50	2.24	2.74	.02	.38	.40
03-30-75	0.20 (as snow in A.M.)								
	(Snow melt)	3,346	6.4	.15	.33	.48	.01	.12	.13
03-31-75	(Snow melt)	6,613							

*Kd = $\frac{\text{ppm in sediment}}{\text{ppm in } H_2O}$

TABLE 22. RAINFALL, RUNOFF AND PESTICIDES IN RUNOFF FOR THE PERIOD 04-01-75 TO 04-13-75

Date	Rain				Watershed 06									
					Runoff	Sediment			Paraquat			Atrazine		
	Duration	2-min max	5-min max	10-min max	Duration	Max flow	No. of samples	Mean	Sed	H_2O	Kd*	Sed	H_2O	Kd
	hr	cm/hr	cm/hr	cm/hr	hr	L/min		g/L	ppm	ppm		ppm	ppm	
04-02-75 to 04-03-75	21.7	.76	.61	.61	(Snow on bare soil, no frost to 60 cm, except on north - facing slopes)									
04-04-75 to 04-07-75	(No precipitation. Nightly freezing formed new frost layer to 15 cm)													
04-08-75	-------- (Snow melt) ----------				8.9	40	6	0.6	10.5	<0.1	106+	1.19	.051	24
04-09-75	-------- (Snow melt) ----------				15.1	24	4	0.5	14.8	<0.1	150+	.94	.050	19
04-10-75	-------- (Snow melt) ----------				13.1	104	6	1.2	15.3	<0.1	155+	1.02	.019	54
04-11-75	-------- (Snow melt) ----------				10.3	40	2	1.0	9.5	<0.1	96+	.63	.015	42
04-12-75	-------- (Snow melt) ----------				6.7	4	1	0.5	25.9	<0.1	262+	1.36	.009	151
04-13-75	-------- (Snow melt) ----------				7.6	12	1	0.6	26.5	<0.1	268+	1.15	.005	230

	Total rain	Total runoff	Total sed	Total paraquat			Total atrazine		
				sed	H_2O	Sum	Sed	H_2O	Sum
	cm	Liters	Kg	g			g		
04-02-75 to 04-03-75	2.26	(33 cm = 13 in snow)							
04-08-75	0.0	9,539	5.4	.06	.94	1.00	.01	.48	.49
04-09-75	0.0	10,925	5.7	.08	1.08	1.17	.01	.54	.55
04-10-75	0.0	23,766	27.7	.42	2.35	2.78	.03	.45	.48
04-11-75	0.0	10,826	10.8	.10	1.07	1.18	.01	.16	.17
04-12-75	0.0	400	0.4	.01	.08	.09	<.01	.01	.01
04-13-75	0.0	2,630	1.6	.04	.26	.30	<.01	.01	.02

*Kd = $\frac{\text{ppm in sediment}}{\text{ppm in } H_2O}$

TABLE 23. RAINFALL, RUNOFF AND PESTICIDES IN RUNOFF FROM WATERSHED 06 FOR UNIQUE RAINFALL EVENTS ON BARE SOIL (04-18-75) AND ON SOIL UNDER CORN COVER (08-21, 22-75)

Date	Rain				Watershed 06									
					Runoff		Sediment		Paraquat			Atrazine		
	Duration	2-min max	5-min max	10-min max	Duration	Max flow	No. of samples	Mean	Sed	H_2O	Kd*	Sed	H_2O	Kd
	hr	cm/hr	cm/hr	cm/hr	hr	L/min		g/L	ppm	ppm		ppm	ppm	
04-18-75	10.8	9.14	7.32	5.03	6.6	10,141	15	15.1	11.9	<0.1	120+	.50	.032	16
08-21-75	6.2	18.29	16.15	12.80	1.6	20,220	8	3.1	24.3	<0.1	246+	.22	.001	215
08-22-75	3.8	3.81	3.05	2.29	1.2	822	4	2.2	15.7	<0.1	159+	.24	.001	243

	Total rain	Total runoff	Total sed	Total paraquat			Total Atrazine		
				Sed	H_2O	Sum	Sed	H_2O	Sum
	cm	Liters	Kg	g			g		
04-18-75	10.9	646,650	9,765	116.1	64.0	180.1	4.92	20.78	25.70
08-21-75	6.1	316,460	1,015	24.7	31.3	56.0	.23	.34	.57
08-22-75	1.8	9,771	21	0.3	1.0	1.3	.01	.01	.02

*Kd = $\frac{\text{ppm in sediment}}{\text{ppm in } H_2O}$

TABLE 24. RAINFALL, RUNOFF AND PESTICIDES IN RUNOFF FROM WATERSHED 07 FOR UNIQUE RAINFALL EVENTS ON BARE SOIL (04-18-75) AND ON SOIL UNDER SOYBEAN COVER (08-21, 22-75)

Date	Rain				Watershed 07									
					Runoff		Sediment		Paraquat			Diphenamid		
	Duration	2-min max	5-min max	10-min max	Duration	Max flow	No. of samples	Mean	Sed	H_2O	Kd*	Sed	H_2O	Kd
	hr	cm/hr	cm/hr	cm/hr	hr	L/min		g/L	ppm	ppm		ppm	ppm	
04-18-75	10.8	9.14	7.32	5.03	4.9	7,862	15	37.0	4.2	<0.1	43+	.14	.025	5
08-21-75	6.2	18.29	16.15	12.80	1.4	11,730	16	4.8	13.0	<0.1	132+	.30	.013	23
08-22-75	3.8	3.81	3.05	2.29	.5	69	2	1.6	12.9	<0.1	130+	.32	.004	77

	Total rain	Total runoff	Total sed.	Total paraquat			Total diphenamid		
				Sed	H_2O	Sum	Sed	H_2O	Sum
	cm	Liters	Kg	g			g		
04-18-75	10.9	470,792	17,411	74.0	46.6	120.6	2.41	11.98	14.39
08-21-75	6.1	219,150	1,062	13.8	21.7	35.5	.32	2.83	3.15
08-22-75	1.8	848	1	< .1	.1	.1	<.01	<.01	<.01

*Kd = $\frac{\text{ppm in sediment}}{\text{ppm in } H_2O}$

snow cover would thaw at the surface during the day but would usually freeze again at night. Soil under drifted snow on intermediate, northerly-facing slopes or under ponded water in central basin areas would thaw less quickly.

On intermediate slopes and in areas of ponding, ice would form at night in the saturated surface soil and then build up on top over a succession of diurnal thawing and freezing cycles. On intermediate slopes, this surface ice and lingering snow which was frequently associated with it served to intercept or divert seepage and runoff from slopes higher up. In bottom areas, surface ice effectively sealed the soil surface so that ponding would occur with even light runoff from surrounding slopes.

The ice layer in lower basin areas persisted until a thaw in mid-March when it disappeared briefly, then formed again. This new ice layer disappeared quickly at the beginning of April as internal drainage was restored by disappearance of a deep frost layer. On intermediate, northerly-facing slopes, surface ice and crusted snow persisted to the middle of April.

Several sequences of runoff, beginning 03-12-75, permit a detailed examination of effects of snow cover, surface icing, and frost on runoff losses of sediments and chemicals under a variety of wintertime weather conditions which are characteristic for the Great Lakes Basin.

The first sequence of weather and watershed conditions is described in Table 13. To start with, the soil was frozen to 46 cm. An earlier aging snow cover (about 0.5 cm on upper slopes and lower basin areas) had been replenished by 5 to 10 cm of fresh snow on 03-06-75 and 03-07-75. This snow would have been equivalent to about 0.5 to 1.0 cm of rain.

Because of the impermeable frost layer over all of the watershed area and the iced soil surface in areas of ponding, snow melt during daylight hours produced net runoff at the catchments on six consecutive days before the last snow disappeared (cf. Tables 13 and 19). On sunny days, melting snow would produce runoff even when air temperature did not rise above freezing (as on 03-14-75).

Air temperatures fell below freezing each night. Thawed surface soil would freeze and ice would form on ponded water. Nevertheless, runoff would continue under the pond ice well into the night, fed by seepage from sloping areas. Even after all snow had disappeared on 03-17-75, runoff continued, fed by seepage from saturated surface soil over frost on sloping areas.

Sediment yields in this sequence were initially low, but increased with daily temperatures and runoff volumes, until snow to provide melt water was nearly gone (Table 19). Increasing sediment pickup reflected decreasing snow cover and increased exposure of surface soil to thawing during the day. Because of the impermeable frost layer, thawed soil remained saturated except on upper slopes which drained quickly by seepage downslope as soon as sources of melt water disappeared. Pickup and movement of sediments could be observed readily wherever runoff occurred over saturated soil.

Chemical concentrations were much greater in the sediment phase than in

the aqueous phase. Kd values were of the order of 10^3 for paraquat and 10^2 for atrazine. The values for paraquat are based on 99 ppb in the aqueous phase, since it was never detected; so the Kd values are undoubtedly low for paraquat. Total loss of chemicals is a function of sediment yield and runoff volume. During these events, major loss of both chemicals was in the aqueous phase.

The second runoff sequence followed a heavy snowfall changing to rain on soil thawed through the plow layer but still frozen in the subsoil (Tables 14 and 20). Ten centimeters of snow in the A.M. of 03-21-75 melted quickly, its disappearance hastened by rain. The total precipitation was 1.47 cm, but no runoff occurred at the catchment until the snow had practically disappeared in early A.M. of 03-22-75.

Three significant features served to delay runoff: (1) interception by the snow cover, (2) the recharge capacity of the thawed plow layer which had had several days to drain by lateral seepage over the impermeable frost layer, and (3) the impoundment capacity of the lower basin where surface ice and ponded water from earlier events had disappeared.

In early A.M. of 03-22-75, runoff due to seepage from the saturated plow layer in sloping areas preceded the first of a series of showers. Since thawed soil was saturated and impoundment areas were already full to overflowing, runoff flows responded promptly to each of the early morning showers on 03-22-75 as well as to each of a series of showers during the night of 03-23 to 03-24-75.

Sediment yields increased progressively over this sequence (Table 20). This is indirect evidence for the extensive redistribution of sediments which occurred on the watershed. Visible sediments were deposited in areas of ponding in segment 5 and in association with lingering snow and ice on northerly and easterly slopes in segments 2 and 3 (Fig. 8).

During the event of 03-23 to 03-24-75, losses of paraquat in sediments exceeded losses in the aqueous phase.

The next two sequences (Tables 15 and 16) occurred during a period of low night temperatures during which a new frost layer formed at the surface while the older deep frost layer continued to recede. By 04-07-75, the new frost layer was 15 cm thick, whereas the old frost layer was encountered only on northerly facing slopes.

During the first of these sequences (Tables 15 and 21), soil on the immediate surface would thaw during the day and freeze again at night. The presence of the new frost layer is reflected in the rather heavy runoff from 0.53 cm of rain on 03-29-75 and in the fact that 2 cm of snow (0.2 cm rain equivalent) produced runoff as it melted over two consecutive days.

On 04-02 and 04-03, 33 cm of snow fell on bare and frozen soil. After a day of high winds and drifting, the snow on upper slopes disappeared quickly under sunny skies, producing runoff which was intercepted by snow on intermediate and lower slopes and by ponding under snow in lower basin areas.

No runoff occurred at catchments until 04-08 (Tables 16 and 22). Runoff volumes and sediment yields increased to a maximum on 04-10, then declined as frost disappeared at points around and within impoundment areas, permitting these areas to drain.

Unique spring and summer events

Except for northerly facing slopes, all snow and surface ice had disappeared and soils had drained and were drying at the surface by 04-18 when a major historic rainfall occurred (Table 17). Useful comparisons can be made between this event and a later major event in August when a vigorous crop canopy was present (Table 18). Due to the magnitude of these events, collection facilities were swamped. Data for the two watersheds in Tables 23 and 24 have been adjusted to allow for some of the difficulties encountered. Sediment yields, in particular, are probably 30% or less of the actual loss. The discrepancy between calculated and real losses is probably greater for watershed 07 than for 06 because drainage away from the collection facilities is more rapid and our visual estimate of after-flume sediments (grossly approximate) was not realistic.

In our Special Memo of October 1976, we stated that undetected sediment losses may have been less at 07 than 06. However, this is inconsistent with our observation that, within the watersheds, sediments were displaced further down the drainageway in 07 than in 06. Also, extreme scouring occurred in segment 0705, and our field log notes that the pipe leading from the Coshocton to the collection house had clogged with sand during the 08-21 event.

Total rainfall and total runoff on 08-21 were about one-half as great as on 04-18, but rainfall intensities and maximum runoff flows were about two-fold greater (Tables 23 and 24). Deep rills and gulleys were cut down central drainageways during both events, but much less sediment was carried to the catchments in the presence of vigorously growing corn and soybeans on 08-21.

Total runoff from the two watersheds during these two events was roughly in proportion to the watershed areas. However, sediment concentrations in the 04-18 runoff from watershed 07 was 2-1/2-fold greater than for 06. Total loss of sediment from the smaller watershed was almost twice as great. This is consistent with our observation that sediments were transported further down the central drainageway in 07 because of the much smaller area where ponding and mid-row sedimentation could occur.

The much lower concentration of paraquat and diphenamid in sediments from 07 during the 04-18 event is consistent with our inference that the proportion of heavier, less adsorptive sediments increases as runoff velocities and sediment loads increase. Objective comparison of sediment yields during the 08-21 event cannot be made because of sampling difficulties, but the lower paraquat in sediment from 07 again reflects the larger proportion of heavier sediments due to more rapid flow of runoff down the narrower central drainageway in 07.

On 08-22, while soils were still well charged with water from the 08-21

event, 1.8 cm of rain produced runoff from both watersheds (Table 18). Total runoff and sediment loss from 07 was proportionately much less in relation to 06 than would have been expected (cf. Tables 23 and 24). Soybeans along the central draw in 07 had lodged severely when their roots were uncovered by deep rills and gulleys cut during the 08-21 event. The fallen vegetation served to slow down runoff and intercept sediments more effectively than the standing crop might have. Rills and gulleys in segment 0702 and upper portions of 0705 were, to a great extent, filled again with sediment during the 08-22 event (cf. Fig. 8).

Corn on 06 did not lodge where deep cross-row rills were cut on 08-21 because of its well established brace roots. Also, cross-row cutting was not as deep on 06 mainly because of the greater opportunity for runoff flows to meander along the E-W axis in segment 0605 and lower portions of 0602. Meandering was promoted by interlacing brace roots which, by intercepting debris and sediments, would effectively block an established rill, forcing runoff to find another channel.

Many of the deep rills cut in watershed 06 on 08-21 were still open after the 08-22 event. Nevertheless, sedimentation in deep rills and along meandering mid-row ponds contributed to greatly reduced sediment losses on 08-22. The 1.8 cm of rain on 08-22 was approximately 1/3 of that on 08-21, but it produced only 1/30 the volume of runoff and 1/50 the sediment loss.

Of course, it must be recognized that the intensity of the rain on 08-22 was about 1/5 as great as on 08-21 (5-minute maxima: 3.05 vs 16.15 cm/hr). Interception by the dense canopies of corn and soybeans and by infiltration into permeable sandy soils would have retained a larger proportion of the 08-21 rainfall on both watersheds.

Summation

Weather sequences which precede a runoff event are important in determining boundary conditions for the event itself. This is particularly true during the colder seasons of the year when precipitation over periods of days or weeks can accumulate as snow on the landscape, and when infiltration and deep percolation are controlled by the distribution of surface ice or of frost within the profile.

A variety of weather and watershed conditions were associated with runoff sequences during winter 1974-75. These have been described in preceding sections. Salient observations should be helpful in interpreting and modelling our data for winter runoff events:

a) The depth and distribution of snow cover reflected effects of wind direction and local relief on patterns of drifting.

b) The depth, age and distribution of snow cover over the watersheds served to moderate the rates of penetration and disappearance of frost in the profile. Direction of slope, in relation to angle of insolation during the warmer part of the

day, was an important factor affecting depth and quality of snow cover and disappearance of surface ice and of frost within the profile.

c) Snow, particularly new snow, can intercept rain and runoff and can delay net runoff from a watershed.

d) Frost in the profile prevents deep percolation of melt water or rain and permits runoff from minor amounts of precipitation.

e) When surface soil thaws on warm or sunny days, it tends to remain saturated and readily suspended in runoff. Upper slopes can drain quickly by seepage as soon as sources of melt water disappear.

f) Nightly freezing forms ice in saturated soil on slopes fed by seepage from above and in areas where ponding occurs during the day. This ice layer is slow to thaw, protects soil on slopes from erosion, but serves to intercept seepage on slopes and to seal the surface in areas of ponding. Under these conditions, seepage from thawed and saturated soil over frost in sloping areas can extend runoff for a time after rain stops or after sources of melt water have disappeared.

g) Sediment pickup from frozen soil is low, but sediment loads in runoff increase as the area exposed to thawing and saturation of surface layers increases.

h) The recharge capacity of thawed soil increases as deep frost layers recede. The quantity of precipitation needed to produce runoff increases accordingly.

i) Sediment yields in runoff collected at catchments provide a basis for identifying events and watershed conditions which produced major redistributions of sediments and chemicals within the watersheds.

The effect of crop cover on runoff and on losses of sediments and chemicals was illustrated by two major historic events in 1975. Runoff volumes and losses were much less in the presence of corn or soybeans in August as compared with an event of longer duration but lesser intensity in April. During a second event of moderate intensity in August, differences in runoff volumes and losses for the two watersheds were related to differences in topography and differences in properties of the crop cover (corn vs soybeans).

At all times, losses of chemicals were a function of runoff volume and sediment yield. The concentration of chemicals was much greater in the sediment phase than in the aqueous phase (apparent Kd values of the order of 10^2 to 10^3). Nevertheless, total loss in the aqueous phase exceeded that in sediments, except for paraquat. The Kd for paraquat was higher than for other chemicals, consistent with its known susceptibility to adsorption. When sediment yields were high, more paraquat moved with sediments than in the

water phase. Total paraquat in runoff was usually much greater than for other chemicals. This is consistent with its much greater persistence in soils. However, calculated losses of paraquat are artifactually high to the extent that actual concentrations in the water phase were less than the 99 ppb input for undetected concentrations.

SECTION VI

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SECTION VII

APPENDIX

TABLE A-1. PROPERTIES OF PESTICIDES USED IN THIS STUDY

Pesticide common name	Trade name	Manufacturer	Chemical name	Formulation properties
paraquat	Paraquat	Chevron	1,1'-Dimethyl-4,4'-bipyridinium ion	dichloride salt 29% a.i. (2 pounds/gal)
diphenamid	Enide	Upjohn	N,N-Dimethyl-2,2 diphenylacetamide	50% wettable powder
trifluralin	TreFlan	Eli Lily	a,a,a-Trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine	44.5% a.i. 4 pounds/gal)
atrazine	AAtrex	Ciba-Geigy Corp.	2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	80% wettable powder